12:13:58 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 04/09/97

Active

Project #: E-19-X50 Cost share #: E-19-336 Rev #: 3
Center # : 10/24-6-R8158-0A0 Center shr #: 10/22-1-F8158-0A0 OCA file #:
Work type : RES
Contract#: DE-FG22-94PC94206 Mod #: M003 Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N CFDA: 81.057
Main project #: PE #:

Project unit: CHEM ENGR Unit code: 02.010.114
Project director(s):
ECKERT C A CHEM ENGR (404)894-2842

Sponsor/division names: US DEPT OF ENERGY / DOE PITTSBURGH - PA
Sponsor/division codes: 141 / 005

Award period: 940901 to 970831 (performance) 971130 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	200,000.00
Funded	0.00	200,000.00
Cost sharing amount		20,000.00

Does subcontracting plan apply ?: N

Title: SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

PROJECT ADMINISTRATION DATA

OCA contact: Jacquelyn L. Bendall 894-4820

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PITTSBURGH ENERGY TECHNOLOGY CENTER
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PITTSBURGH, PA 15236-0940

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : DOE supplemental sheet
Equipment title vests with: Sponsor GIT X
PRIOR APPROVAL REQUIRED IF OVER $500.00 AND NOT IN APPORVED PROPOSAL BUDGET.
Administrative comments -
MODIFICATION NO. M003 IDENTIFIES OAK RIDGE FINANCIAL SERVICE CENTER AS THE PAYMENT OFFICE FOR THIS GRANT EFFECTIVE 4-1-97.

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/ 6

Closeout Notice Date 05-DEC-1997

Project Number E-19-X50 Doch Id 34392

Center Number 10/24-6-R8158-0A0

Project Director ECKERT, CHARLES

Project Unit CHEM ENGR

Sponsor US DEPT OF ENERGY/DOE PITTSBURGH - PA

Division Id 3494

Contract Number DE-FG22-94PC94206 Contract Entity GTRC

Prime Contract Number

Title SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Effective Completion Date 31-AUG-1997 (Performance) 30-NOV-1997 (Reports)

Closeout Action:	Y/N	Date Submitted
inal Invoice or Copy of Final Invoice	Y	30-SEP-1997
inal Report of Inventions and/or Subcontracts	Y	
overnment Property Inventory and Related Certificate	Y	26-SEP-1997
lassified Material Certificate	N	
elease and Assignment	N	
ther	N	

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Distribution Required:

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OTE: Final Patent Questionnaire sent to PDPI

DOE F 1430.22
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OMB Control No.
1910-1400
Burden Disclosure
Statement on Back

U.S. DEPARTMENT OF ENERGY
NOTICE OF ENERGY RD&D PROJECT

1. DOE CONTRACT OR GRANT NUMBER DE-FG22-94PC94206

   X ☒ New contract ☐ Continuation/Revision

2. A. NAME OF PERFORMING ORGANIZATION GEORGIA INSTITUTE OF TECHNOLOGY

   B. Department or Division CHEMICAL ENGINEERING

   C. Street Address 778 ATLANTIC DR.

   City ATLANTA State GA Zip 30332

   D. Type of Performing Organization (circle only one two-letter code)

   CU–College, university, or trade school
   EG–Electric or gas utility
   FF–Federally funded RD&D centers or laboratory operated for agency of US government
   IN–Private industry
   NP–Foundation or laboratory not operated for profit
   ST–Regional, state, or local government facility
   TA–Trade or professional organization
   US–Federal Agency
   XX–Other

3. PRINCIPAL OR SENIOR INVESTIGATOR

   A. Last ECKERT First CHARLES MI A

   B. Phone: Commercial (404) 853-9344 FTS

4. DOE SPONSORING OFFICE OR DIVISION DOE PITTSBURGH - PA 141/005

5. TITLE OF PROJECT

   SUPERCRITICAL FLUID REACTION FOR COAL PROCESSING

6. DESCRIPTIVE SUMMARY (limit to 200 words)

Utilizing reactants which closely resemble the organic sulfur and nitrogen components of coal, we propose to develop a method to tailor chemical reaction in supercritical fluid (SCF) solvents for the specific application of coal desulfurization and denitrogenation. We shall make kinetic and thermodynamic measurements on the reactin systems to elucidate the intermolecular interactins affecting the reaction transition states in SCFs. These data shall be used to develop mathematical models that will be used to predict kinetic solvent effects in SCF solvents.

7. RESPONDENT INFORMATION. List name and address of person filling out this form. Give telephone number and extension where person can be reached. Record the date this form was completed or updated. This information will not be published.

Last VINCENT First MICHAEL MI F

Address 778 ATLANTIC DR.

City ATLANTA State GA Zip 30332

Phone (404) 894-6766 Date NOV. 11, 1994

HAZARDOUS SUBSTANCE PLAN

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FR22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Substance	CAS Number	EPA Hazardous Waste Number	EPA Hazard Code	Quantity, kg
Acetone	67-64-1	U002	I	0.001
Acetonitrile	75-05-8	U003	I, T	0.001
Ethane, 1,1,1-trichloro	71-65-6	U226	T	0.001
Chloroform	67-66-3	U044	T	0.001
Tetrahydrofuran	109-99-9	U213	I	0.001

Anticipated Hazardous Waste Transporter and/or Contractor

Georgia Institute of Technology awards contracts for the disposal of waste through a bidding process. Firms who have handled our waste in the past include, but are not limited to: ECOFLOW, Laidlaw, and Advanced Environmental Technology Corporation.

Anticipated Treatment Method

The type of waste generated in this project (organic materials with no heavy metals) is typically disposed of by high temperature incineration or fuel blending.

E·19-X50
16

HAZARDOUS WASTE REPORT

No hazardous waste was produced or consumed during this work.

m RA-427 **U.S. DEPARTMENT OF ENERGY** OMB NO. 038-R0180

UNIVERSITY CONTRACTOR, GRANTEE AND COOPERATIVE AGREEMENT RECOMMENDATIONS FOR ANNOUNCEMENT AND DISTRIBUTION OF DOCUMENTS

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Report No. OE/PC/94206 - 1	3. Title SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING
ject No. E - FG22-- 94PC 94206	

of Document ("X" one)

. Scientific and technical report

. Conference paper:

Title of conference _____

Date of conference _____

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mitted by Name and Position (Please print or type)

arles A. Eckert, Professor of Chemical Engineering

anization

orgia Institute of Technology

nature Date 10/27/94

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nt Clearance ("a" one)

a. DOE patent clearance has been granted by responsible DOE patent group.

b. Report has been sent to responsible DOE patent group for clearance.

QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Period Covered by Report: September 1, 1994 - September 30, 1994

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which closely resemble the organic sulfur and nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal desulfurization and denitrogenation. Diels-Alder reactions involving such compounds have been extensively studied and characterized in liquids. However, there is very little understanding of such reactions in SCF's. We are developing an approach which will allow optimum design of coal desulfurization and denitrogenation processes.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general (Brennecke & Eckert 1989: Ekart; et. al. 1991: Johnston; et. al. 1989), as well as in many specific applications to environmental control (Eckert; et. al. 1986: Leman; et. al. 1990).

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

The first month of work consisted of refurbishing the requisite reactors, which consisted of reassembling and pressure testing the reactors and mixing vessels. Experimental protocols are in the process of being developed for the reactions and product analyses.

THERMODYNAMIC MEASUREMENTS

All the work completed thus far involved the installation and evaluation of the most recent software upgrades for the Lee Scientific Supercritical Fluid Chromatograph. Experimental and operational protocols are in the process of being developed for the preparation of cosolvent mixtures and the operation of the new software.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

Reaction kinetics under SCF conditions have been investigated in a limited number of studies. Most experimental studies have shown extreme effects of the solvent environment. The volume of activation, $\Delta v^{\ddagger}$, (normally 10-30 $\frac{cm^3}{mole}$ in liquids), may be quite large; for example, Johnston and Haynes (1987) reported $\Delta v^{\ddagger} = -6000 \frac{cm^3}{mole}$ for a decomposition reaction.

The extreme effects of SCF's on reaction rates is almost wholly due to the unusual solvent properties and their unique interactions with reactants and transition states. SCF solutions are almost always highly asymmetric systems. This asymmetry precludes many classical treatments, which have embedded in them some manifestation of corresponding states theory.

The unusual behavior of reactions in these asymmetric SCF's is due to anomalous local behavior. Extreme solvation of the transition state gives the large negative partial molar volumes of solutes in the activation volume. Local composition augmentation exists also, and will have a strong effect on chemical kinetics as well. At present this effect is not yet well quantified.

Evaluation of solution kinetics using the transition state theory (Eckert & Boudart 1963: Evans & Polanyi 1935: Eyring 1935: McCabe & Eckert 1974) permits the transformation of a rate problem into a thermodynamic equilibrium problem. The rate constant, k_x, is related to the partial molar volume of activation and pressure by Equation (1).

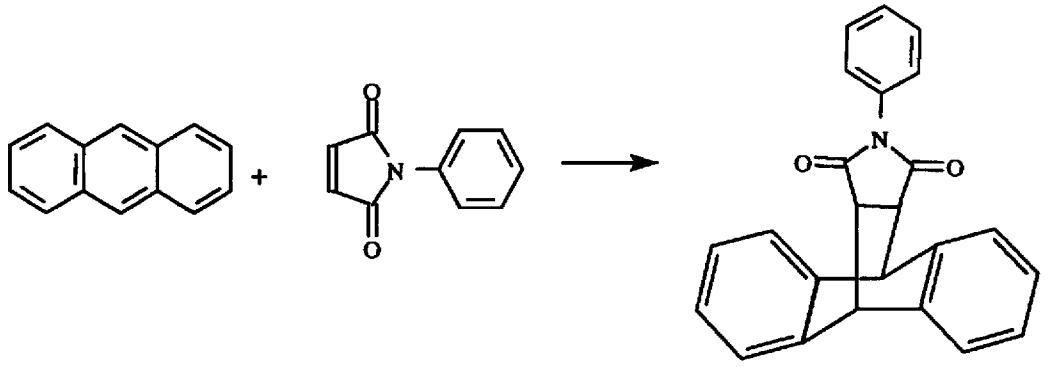
$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT} \qquad (1)$$

The partial molar volume of activation, $\Delta v^{\ddagger}$, is given in terms of partial molar volumes in solution,

$$\Delta v^{\ddagger} = v_M - \sum v_{reactants} \qquad (2)$$

where v_M is the partial molar volume of the transition state. Typically, volume of activation information has been used to elucidate the structure and properties of reaction transition state, to understand mechanisms, regiochemistry, and related effects (Eckert 1972: leNoble 1967: Weale 1967). We shall investigate the kinetics of a well characterized reaction (Diels-Alder), for which we have detailed knowledge of the structure and properties of the transition state. With the transition state well characterized the kinetics of the reaction will give detailed information regarding the structure of the supercritical fluid.

We shall begin by studying the reaction of anthracene and N-phenyl maleimide



in propane. Reactions shall be run in a well stirred batch reactor. The batch reactor has two windows oriented at 90° with a stir bar well in the bottom. The N-phenyl maleimide shall be in excess and the extent of the reaction shall be followed by observing the disappearance of the anthracene via UV fluorescence. Due to the sensitivity of UV fluorescence, very dilute concentrations (on the order of 10^{-8} mole fraction) of anthracene shall be required. These preliminary experiments will allow us to define the conditions for the detailed kinetics study in the continuous reactors.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's (Ekart; et. al. 1993), which is a variation on several previous successful techniques (Bartle; et. al. 1990a: Bartle; et. al. 1990b: Shim & Johnston 1991: Smith; et. al. 1987). The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^S}{V^S} \right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^{∞}, and partial molar enthalpy, h_i^{∞}, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^{\infty}}{\partial P}\right)_T = v_i^{\infty} \qquad (5)$$

$$RT\left(\frac{\partial \ln \phi_i^{\infty}}{\partial T}\right)_P = -\frac{h_i^{\infty}}{T} \qquad (6)$$

Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

We shall begin by measuring the capacity factor of anthracene and N-phenyl maleimide in pure supercritical propane. Isotherms and isobars shall be investigated to cover the ranges of interest.

SUMMARY

We are completing the preliminary work required to study the kinetics and thermodynamics of desulfurization and denitrogenation reactions in supercritical fluids.

Future work will investigate the Diels-Alder reactions of anthracene with N-phenyl maleimide in supercritical propane. The effect of cosolvents on the kinetics and thermodynamics of the above reaction will also be investigated. Batch reactions shall be used to scout the above experiments and the detailed kinetics determined via a continuous tubular reactor. The thermodynamics of the reactions shall be determined using a supercritical fluid chromatographic technique.

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DA-427 **U.S. DEPARTMENT OF ENERGY** OMB NO. 038-R0190

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Report No.	2. Title
DE/PC/94206 - 1	SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING
Contract No. - FG22 - 94PC 94206	

Type of Document ("X" one)

Scientific and technical report

Conference paper:

Title of conference _____

Date of conference _____

Exact location of conference _____

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Submitted by (Name and Position (Please print or type))

Charles A. Eckert, Professor of Chemical Engineering

Organization

Georgia Institute of Technology

Signature

Date 1/31/95

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Patent Clearance ("X" one)

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Period Covered by Report: October 1, 1994 - December 31, 1994

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which closely resemble the organic sulfur and nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal desulfurization and denitrogenation. Diels-Alder reactions involving such compounds have been extensively studied and characterized in liquids. However, there is very little understanding of such reactions in SCF's. We are developing an approach which will allow optimum design of coal desulfurization and denitrogenation processes.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

We have carried out significant design improvements on our custom-built high-pressure fluorescence spectrometer. As soon as a few more parts arrive the upgraded version will be available for use.

THERMODYNAMIC MEASUREMENTS

The repairs on the Lee Scientific Supercritical Fluid Chromatograph have been completed. We are in the process of beginning the capacity factor determination of anthracene and N-phenyl maleimide in pure ethane and pure carbon dioxide.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

Reaction kinetics under SCF conditions have been investigated in a limited number of studies. Most experimental studies have shown extreme effects of the solvent environment. The volume of activation, $\Delta v^{\ddagger}$, (normally 10-30 $\frac{cm^3}{mole}$ in liquids), may be quite large; for example, Johnston and Haynes (1987) reported $\Delta v^{\ddagger} = -6000 \frac{cm^3}{mole}$ for a decomposition reaction.

The extreme effects of SCF's on reaction rates is almost wholly due to the unusual solvent properties and their unique interactions with reactants and transition states. SCF solutions are almost always highly asymmetric systems. This asymmetry precludes many classical treatments, which have embedded in them some manifestation of corresponding states theory.

The unusual behavior of reactions in these asymmetric SCF's is due to anomalous local behavior. Extreme solvation of the transition state gives the large negative partial molar volumes of solutes in the activation volume. Local composition augmentation exists also, and will have a strong effect on chemical kinetics as well. At present this effect is not yet well quantified.

Evaluation of solution kinetics using the transition state theory [Eyring, 1935; Evans, 1935; Eckert, 1963; McCabe, 1974] permits the transformation of a rate problem into a thermodynamic equilibrium problem. The rate constant, k_x, is related to the partial molar volume of activation and pressure by Equation (1).

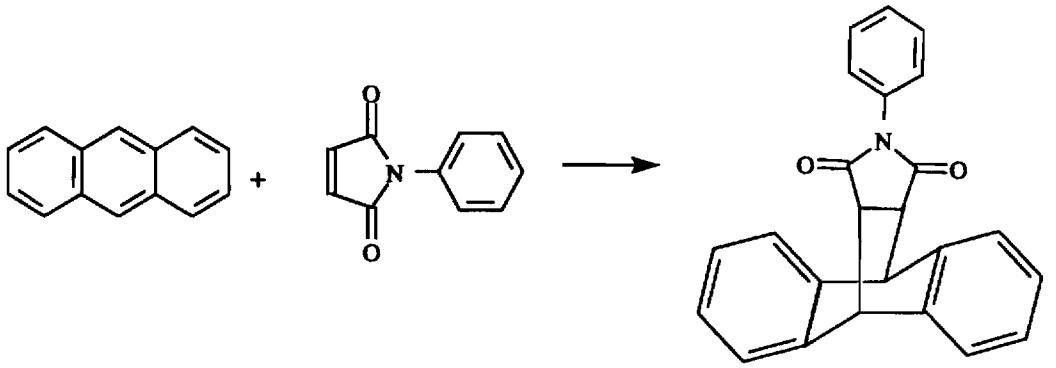
$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT} \qquad (1)$$

The partial molar volume of activation, $\Delta v^{\ddagger}$, is given in terms of partial molar volumes in solution,

$$\Delta v^{\ddagger} = v_M - \sum v_{reactants} \qquad (2)$$

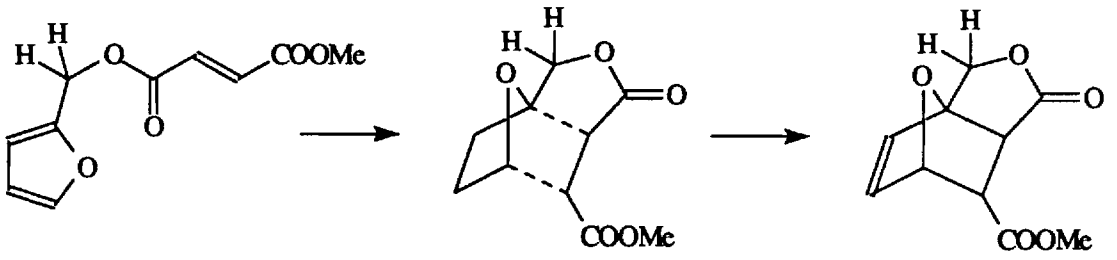
where v_M is the partial molar volume of the transition state. Typically, volume of activation information has been used to elucidate the structure and properties of reaction transition state, to understand mechanisms, regiochemistry, and related effects [Weale, 1967; leNoble, 1967; Eckert, 1972]. We shall investigate the kinetics of a well characterized reaction (Diels-Alder), for which we have detailed knowledge of the structure and properties of the transition state. With the transition state well characterized the kinetics of the reaction will give detailed information regarding the structure of the supercritical fluid.

We shall begin by studying the reaction of anthracene and N-phenyl maleimide



in propane. Reactions shall be run in a well stirred batch reactor. The batch reactor has two windows oriented at 90° with a stir bar well in the bottom. The N-phenyl maleimide shall be in excess and the extent of the reaction shall be followed by observing the disappearance of the anthracene via UV fluorescence. Due to the sensitivity of UV fluorescence, very dilute concentrations (on the order of 10^{-8} mole fraction) of anthracene shall be required.

We shall also begin preliminary work investigating the kinetics of the solvent sensitive intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate to form (±)-(3aR,6S,7S,7aS)-Methyl 1,6,7,7a-Tetrahydro-1-oxo-3H-3a,6-epoxyisobenzofuran-7-carboxylate [Jung, 1991] shown below:



The intramolecular Diels-Alder reaction shall be run in ethane and carbon dioxide. The reactor shall be a well stirred high pressure batch reactor. The extent of reaction shall be followed by oberving the appearance of products using FT-IR spectroscopy.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^S}{V^S} \right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P} \right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T} \right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

We shall begin by measuring the capacity factor of anthracene and N-phenyl maleimide in pure supercritical propane. The capacity factor of (E)-(2-Furanyl)methyl Methyl 2-butenedioate shall be measured in pure ethane and pure carbon dioxide. Isotherms and isobars shall be investigated to cover the ranges of interest.

SUMMARY

We have carried out significant design improvements on our custom-built high-pressure fluorescence spectrometer. As soon as a few more parts arrive the upgraded version will be available for use. We have completed the preliminary work required to study the thermodynamics of desulfurization and denitrogenation reactions in supercritical fluids.

Future work will investigate the Diels-Alder reactions of anthracene with N-phenyl maleimide in supercritical propane and the intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate. The effect of cosolvents on the kinetics and thermodynamics of the above reactions will also be investigated. The thermodynamics of the reactions shall be determined using a supercritical fluid chromatographic technique.

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Period Covered by Report: January 1, 1995 - March 31, 1995

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which closely resemble the organic sulfur and nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal desulfurization and denitrogenation. Diels-Alder reactions involving such compounds have been extensively studied and characterized in liquids. However, there is very little understanding of such reactions in SCF's. We are developing an approach which will allow optimum design of coal desulfurization and denitrogenation processes.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

We have started characterizing the reaction of anthracene with maleimide and N-methyl maleimide, separately, in liquid solvents. Obtaining reaction rate data in liquids (potential future cosolvents) has two objectives. The first objective is to verify our fluorescence technique. The second objective is to obtain the kinetic parameters required for future work in cosolvent modified supercritical fluid systems.

We have measured the rate constant of the intramolecular Diels-Alder reaction in liquid acetonitrile and reproduced the results of Jung, 1991.

THERMODYNAMIC MEASUREMENTS

The capacity factor determination for anthracene in supercritical ethane has been completed at 35°C from 75 to 200 bar. The results are reported as raw capacity factor data and transformed into density data as well. Please see the Appendix for details of work completed thus far.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

Reaction kinetics under SCF conditions have been investigated in a limited number of studies. Most experimental studies have shown extreme effects of the solvent environment. The volume of activation, $\Delta v^{\ddagger}$, (normally 10-30 $\frac{cm^3}{mole}$ in liquids), may be quite large; for example, Johnston and Haynes (1987) reported $\Delta v^{\ddagger} = -6000 \frac{cm^3}{mole}$ for a decomposition reaction.

The extreme effects of SCF's on reaction rates is almost wholly due to the unusual solvent properties and their unique interactions with reactants and transition states. SCF solutions are almost always highly asymmetric systems. This asymmetry precludes many classical treatments, which have embedded in them some manifestation of corresponding states theory.

The unusual behavior of reactions in these asymmetric SCF's is due to anomalous local behavior. Extreme solvation of the transition state gives the large negative partial molar volumes of solutes in the activation volume. Local composition augmentation exists also, and will have a strong effect on chemical kinetics as well. At present this effect is not yet well quantified.

Evaluation of solution kinetics using the transition state theory [Eyring, 1935; Evans, 1935; Eckert, 1963; McCabe, 1974] permits the transformation of a rate problem into a thermodynamic equilibrium problem. The rate constant, k_x, is related to the partial molar volume of activation and pressure by Equation (1).

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT} \qquad (1)$$

The partial molar volume of activation, $\Delta v^{\ddagger}$, is given in terms of partial molar volumes in solution,

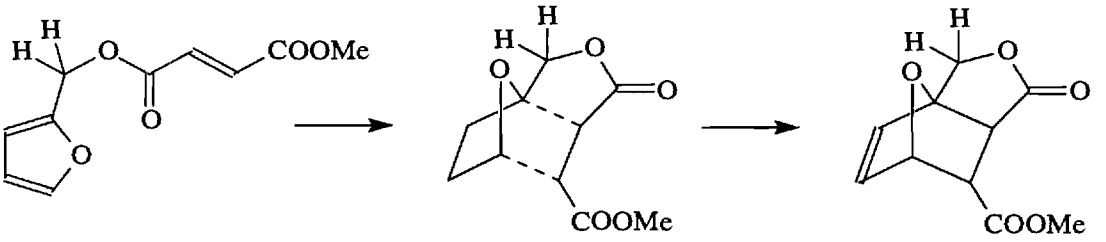
$$\Delta v^{\ddagger} = v_M - \sum v_{reactants} \qquad (2)$$

where v_M is the partial molar volume of the transition state. Typically, volume of activation information has been used to elucidate the structure and properties of reaction transition state, to understand mechanisms, regiochemistry, and related effects [Weale, 1967; leNoble, 1967; Eckert, 1972]. We shall investigate the kinetics of a well characterized reaction (Diels-Alder), for which we have detailed knowledge of the structure and properties of the transition state. With the transition state well characterized the kinetics of the reaction will give detailed information regarding the structure of the supercritical fluid.

We shall continue studying the reaction of anthracene and N-phenyl maleimide

in liquids. We shall also run this reaction in supercritical propane. Reactions shall be run in a well stirred batch reactor. The batch reactor has two windows oriented at 90° with a stir bar well in the bottom. The N-phenyl maleimide shall be in excess and the extent of the reaction shall be followed by observing the disappearance of the anthracene via UV fluorescence. Due to the sensitivity of UV fluorescence, very dilute concentrations (on the order of 10^{-8} mole fraction) of anthracene shall be required.

We shall also begin preliminary work investigating the kinetics of the solvent sensitive intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate to form (±)-(3aR,6S,7S,7aS)-Methyl 1,6,7,7a-Tetrahydro-1-oxo-3H-3a,6-epoxyisobenzofuran-7-carboxylate [Jung, 1991] shown below:



This intramolecular Diels-Alder reaction shall be run in liquid solvents first. The solvents include, but are not limited to, acetonitrile, dimethyl sulfoxide, acetone, and methanol. The reactor shall be a narrow path length IR transparent cell. We also plan to run at least one reaction in supercritical carbon dioxide this coming quarter. The extent of reaction shall be followed by oberving the appearance of product and disappearance of reactant using FT-IR spectroscopy.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F V^S}{V^S} \right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P} \right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T} \right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

We shall begin by measuring the capacity factor of anthracene and N-phenyl maleimide in pure supercritical ethane. The capacity factor of (E)-(2-Furanyl)methyl Methyl 2-butenedioate shall be measured in pure pure carbon dioxide. Isotherms and isobars shall be investigated to cover the ranges of interest.

SUMMARY

We have completed the preliminary work required to study the kinetics and thermodynamics of desulfurization and denitrogenation reactions in supercritical fluids. We have begun characterizing the reactions in liquids at ambient pressures. This initial work is required to establish the credibility of our proposed experimental techniques.

Future work will investigate the Diels-Alder reactions of anthracene with N-phenyl maleimide in liquids and supercritical propane and the intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate in liquids and supercritical carbon dioxide. The effect of cosolvents on the kinetics and thermodynamics of the above reactions will also be investigated. The thermodynamics of the reactions shall be determined using a supercritical fluid chromatographic technique.

APPENDIX

Introduction

Through transition state kinetics, thermodynamic data can elucidate relative reaction rates. Thermodynamic data become even more important when the kinetics are run at high pressures. For studying the kinetics of anthracene Diels-Alder reactions in supercritical fluids, we have investigated the solubilities of anthracene in supercritical ethane using a supercritical fluid chromatograph.

Theory

The solubility of a solid in a supercritical fluid can be measured by supercritical fluid chromatography (Ekart *et al.*,. 1993, Suleiman *et al.*, 1993). The solubility is inversely related to the capacity factor as shown in equation 1.

$$y = \left[\frac{P^{sat} V^S}{H^0 V^m v^s} \exp\left(\frac{v\ (P\ - P^{sat})}{RT} \right) \right] \frac{v^m}{k} = \left[C(T) \right] \frac{v^m}{k} \qquad (1)$$

where y is the mole fraction of the solid in the supercritical phase, P^{sat} is the sublimation pressure of the solid, v^S and v^m are the molar volumes of the stationary and mobile phases in the chromatographic column, V^S and V^m are the physical volumes of the stationary and mobile phases, H_i is the Henry's constant of the solute in the stationary phase. The capacity factor, k, is defined as

$$k = \frac{t_r - t_0}{t_0} \qquad (2)$$

where t_r is the retention time of the solute and t_O is the unretained time.

The expression (1) is simplified by assuming the terms in the brackets are only a function of T. From that assumption, one independently measured solubility can be used to determine that constant. The chromatograph can then be used to measure the solubilities for the rest of the isotherm.

Experimental

The supercritical fluid chromatograph used has been described in Ekart *et al.*, 1993. Briefly, the supercritical chromatograph used was a Lee Scientific Model 600-D with 137 mL syringe pump and UV detector. The column was a SB-Methyl-100 (50 μm × 10 m, film thickness 0.25 μm) from Lee Scientific. Pressure was measured at the entrance of the column using a Heise pressure gauge accurate to ±0.1 psi and controlled to ±0.2 psi. Temperature was measured with a Hart Scientific model 1006 digital thermometer and controlled to ±0.05°C.

CP grade ethane (99 percent) was purchased from Matheson Gas Products. Anthracene and pentane were purchased from Aldrich Chemical Co. All materials were used as received.

Approximately 20 μg of anthracene was injected in a solution of pentane. The retention times were measured using the UV detector. The retention time of pentane was used as t_0. Experiments were conducted at 35°C and pressures from 75 to 200 bar.

Results

The capacity factors measured are plotted versus ethane density in Figure 1. Ethane densities were calculated from a modified Benedict-Webb-Rubin equation of state (Younglove and Ely, 1987). The solubility measurements from Johnston *et al.* (1982) were used to evaluate the constant in equation 1. The calculated solubilites are shown in Figure 2 with those of Johnston *et al.* The complete data set can be found in the appendix.

Figure 1. Capacity Factors of Anthracene in Supercritical Ethane

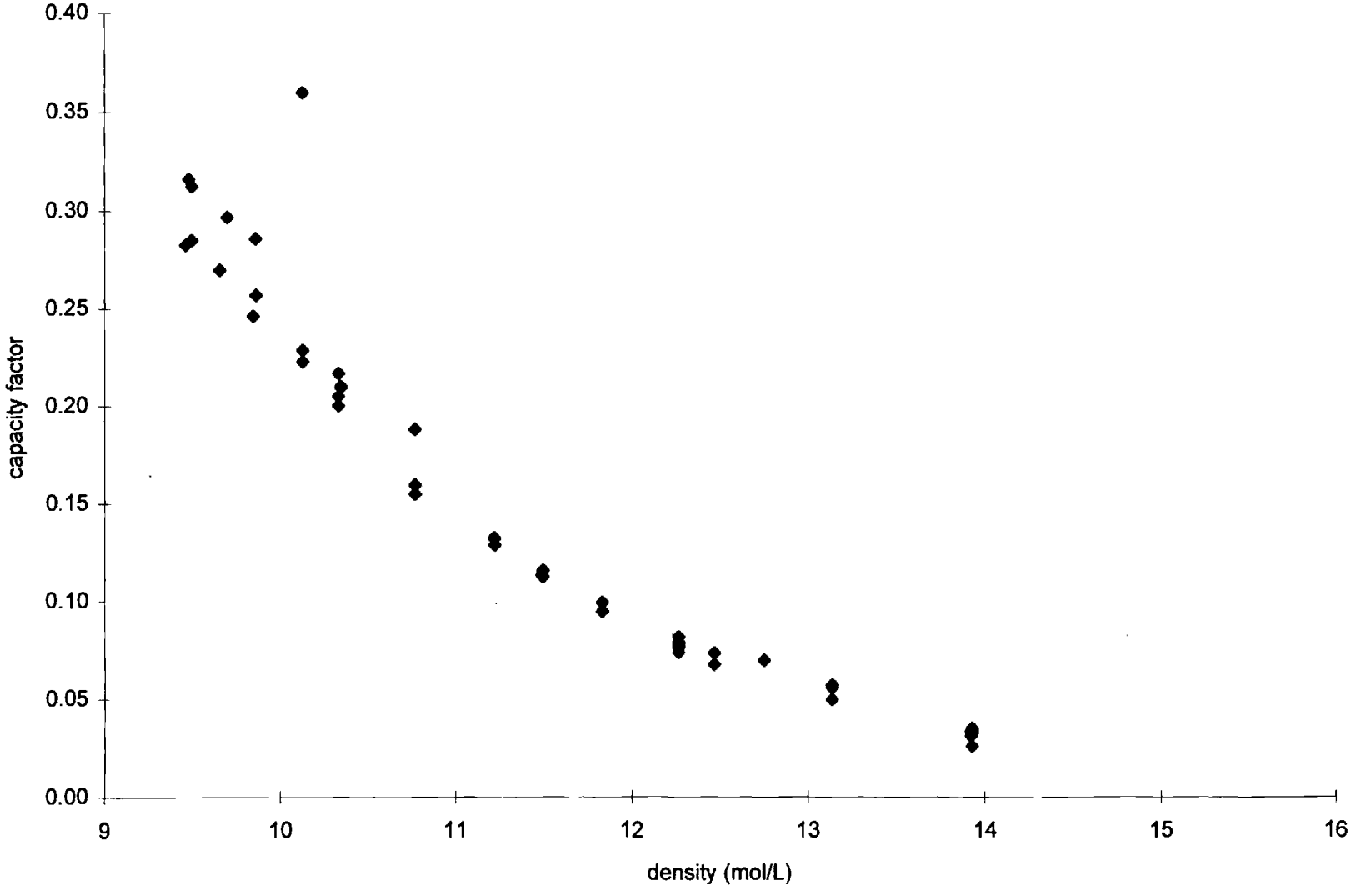
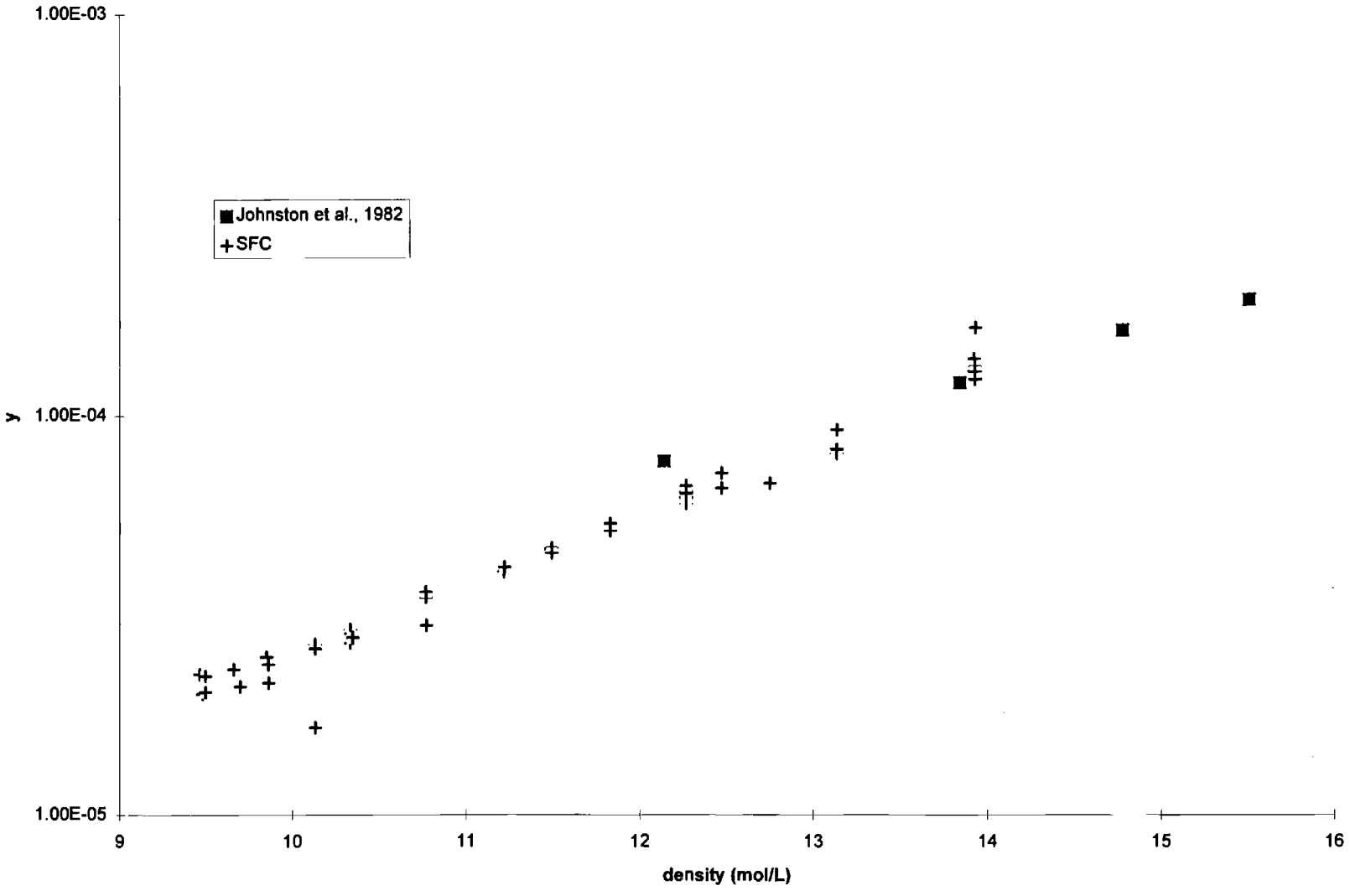


Figure 2. Solubility of Anthracene in Ethane from Supercritical Fluid Chromatagraphy



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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Period Covered by Report: April 1, 1995 - June 30, 1995

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which closely resemble the organic sulfur and nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal desulfurization and denitrogenation. Diels-Alder reactions involving such compounds have been extensively studied and characterized in liquids. However, there is very little understanding of such reactions in SCF's. We are developing an approach which will allow optimum design of coal desulfurization and denitrogenation processes.

OBJECTIVES

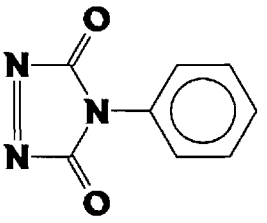
The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

The kinetic measurements of anthracene with a dienophile in liquid solvents are complete. The reaction rates of several dienophiles were measured in liquid solvents, namely n-phenylmaleimide, maleimide, and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). PTAD is two orders of magnitude more reactive than the other candidates, and has been selected as the dienophile for this Diels-Alder system.



4-phenyl-1,2,4-triazoline-3,5-dione (PTAD)

The fluorescence spectroscopic equipment which is to be employed in the supercritical phase of the project was used to obtain kinetic and thermodynamic data for the Diels-Alder reaction of anthracene and PTAD in liquid acetonitrile. The values obtained for the enthalpies and entropies of activation match those reported by A. I. Konvalov (1979), who measured the kinetics of the identical chemical system using UV spectroscopy. This agreement validates our fluorescence equipment and methods for this task.

Some preliminary measurements of the kinetics of anthracene and PTAD in supercritical CO2 have been completed. Results confirm that this reaction does run in the supercritical phase, and that the reaction has a conveniently short half-life. However, the solubility of PTAD in supercritical CO2 is low, necessitating the acquisition of accurate solubility data for the temperatures and pressures at which the reaction will be run. Apparatus for

measuring the solubility of solids in pure and mixed supercritical solvents has been assembled. The design follows that of K. P. Johnston (1987). The solubility equipment is currently being calibrated.

THERMODYNAMIC MEASUREMENTS

Capacity factor measurements for anthracene in various supercritical fluids have been completed along one isotherm and one isobar. The fluids for which data has been collected are ethane, and CO2.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

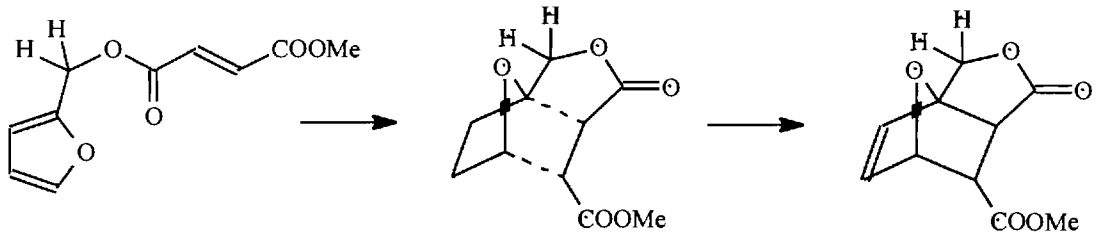
We shall complete the calibration of the new solubility equipment and obtain data for the solubility of PTAD in supercritical CO2 over an appropriate range of temperatures and pressures.

We shall begin to collect the data needed to quantify the intermolecular interactions affecting reaction transition states for the Diels-Alder reaction of anthracene and PTAD in supercritical CO2. Kinetic data will be collected at various pressures along several isotherms for the reaction in pure CO2. The data will be correlated with respect to the following equation:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT}$$

This correlation will provide values for the partial molar volume of activation at different temperatures.

We shall also continue preliminary work investigating the kinetics of the solvent sensitive intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate (FMMB) to form (±)-(3aR,6S,7S,7aS)-Methyl 1,6,7,7a-Tetrahydro-1-oxo-3H-3a,6-epoxyisobenzofuran-7-carboxylate [Jung, 1991 #29] shown below:



The preliminary work mentioned above is comprised of the completion of an IR transparent high pressure sample cell which has recently been customized to fit within our FTIR spectrograph.

As noted above, this intramolecular Diels-Alder reaction has been run successfully in liquid acetonitrile using UV spectroscopy, but we chose not to run this reaction in supercritical CO2 in the FTIR until the new sample cell had been completed. The new cell will be used this quarter to run the above reaction in liquid solvent, and also supercritical CO2. The solvents to be used include, but are not limited to, acetonitrile, dimethyl sulfoxide, acetone, and methanol.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^s}{V^s}\right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P}\right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T}\right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

We shall begin measuring the capacity factor of PTAD in pure supercritical CO2. The capacity factor of (E)-(2-Furanyl)methyl Methyl 2-butenedioate shall be measured in pure carbon dioxide. Isotherms and isobars shall be investigated to cover the ranges of interest.

SUMMARY

We have completed the liquid phase work of the reaction of several dienophiles with anthracene in acetonitrile. Several dienophiles were tested, and PTAD was selected as the dienophile best suited to our needs. Our fluorescence spectroscopic techniques were used to obtain the kinetic data for PTAD with anthracene, and the values obtained for the enthalpies and entropies of transition closely match those reported by A. I. Konvalov (1979). We have constructed equipment necessary for the measurement of the solubility of PTAD in supercritical CO2, and are currently calibrating the equipment. Some preliminary studies of the reaction of PTAD with anthracene in supercritical CO2 have confirmed that the reaction runs, and that it possesses a conveniently short half-life.

Future work will investigate the Diels-Alder reactions of anthracene PTAD in supercritical CO2 and the intramolecular Diels-Alder reaction of (E)-(2-Furanyl)methyl Methyl 2-butenedioate (FMMB) in supercritical carbon dioxide. The effect of cosolvents on the kinetics and thermodynamics of the above reactions will also be investigated. The thermodynamics of the reactions shall be determined using a supercritical fluid chromatographic technique.

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 853 - 9344

Initiation Date: September 1, 1994

Period Covered by Report: July 1, 1995 - September 31, 1995

ABSTRACT

A number of possible Diels-Alder reactive systems involving anthracene (diene) in supercritical solvent were proposed at the outset of research. Scouting experiments designed to select out the optimum reactive system from among the candidate dienophiles and solvents have been completed. The nitrogen bearing compound 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) has demonstrated superior reactivity and sensitivity to cosolvent additions and has been selected as dienophile. A convenient half-life of reaction between PTAD and anthracene is obtained at temperatures in the neighborhood of 50 C. Carbon dioxide has been selected as the solvent because of its convenient critical properties, and also to optimize the safety of the experiments. In the process of completing these scouting experiments, the experimental apparatus that will be used to obtain kinetic data for calculation of partial molar volumes of the reaction transition state has also been optimized.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

KINETIC MEASUREMENTS

The fluorescence spectroscopic equipment which is to be employed in the supercritical phase of the project was used to obtain kinetic and thermodynamic data for the Diels-Alder reaction of anthracene and PTAD in liquid acetonitrile. Results of selected runs are presented as Figure 1 in the Appendix. The observed first order rate constant for this system normalized to 25 C was obtained using these data, and was found to be 0.35 1/Ms. A. I. Konvalov (1979) measured the kinetics of the identical chemical system using UV spectroscopy and obtained an observed first order rate constant of 0.32 1/Ms. This agreement validates our fluorescence equipment and methods for this task.

As mentioned in a previous report, some preliminary measurements of the kinetics of anthracene and PTAD in supercritical CO2 have been completed. Results confirmed that this reaction does run in the supercritical phase, and that the reaction has a conveniently short half-life, but that the solubility of PTAD in supercritical CO2 is low. This low solubility necessitates the acquisition of accurate solubility data for the temperatures and pressures at which the reaction will be run. Once accurate solubility values have been determined, the supercritical phase of the project will begin. PTAD will be introduced into the reaction cell in quantities well below its solubility limit in order to avoid possible distortion of results that could occur if the experiments are performed with excess solid PTAD in the bottom of the reaction cell.

There are two paths by which distortion of results could occur in response to the presence of excess solid PTAD. The first is by possible solubility enhancement in the presence of anthracene. Solubility limits will be measured for PTAD in CO_2 with no anthracene present. If solid PTAD is present in the cell during an actual reaction the concentration of PTAD in the reaction mixture should then be the saturation value. But it is possible that under actual reaction conditions the saturation solubility of PTAD in CO_2

could be enhanced by the presence of anthracene. In this case, the actual saturation concentration of PTAD in the reaction mixture would be greater than that measured using the solubility apparatus. This would lead to incorrect values of the observed first order rate constant for that reaction, and this in turn would lead to incorrect values for partial molar volumes of the transition state.

The second path by which distortion of results could occur in response to the presence of excess solid PTAD involves the possibility of reaction at the solid-CO_2 interface. In this case, the disappearance of anthracene - which produces the measured signal in fluorescence spectroscopy - would proceed by a complex mechanism involving both supercritcal phase kinetics and solid kinetics. This event would also have the effect of distorting the measured value of the observed first order rate constant.

Apparatus for measuring the solubility of solids in pure and mixed supercritical solvents has been assembled. The design follows that of K. P. Johnston (1987). The solubility equipment has been calibrated and is ready for use in determining saturation solubilities for PTAD in supercritical CO2 at the temperatures and pressures that will be needed for the analysis of partial molar volumes in the transition state.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

We shall use the new solubility equipment to obtain data for the solubility of PTAD in supercritical CO2 over an appropriate range of temperatures and pressures.

We shall complete collection of kinetic data for the system PTAD with anthracene in supercritical CO_2. Kinetic data will be collected at various pressures along at least one isotherm for the reaction in pure CO2. The data will be correlated with respect to the following equation:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\mp}}{RT}$$

If the quantification of partial molar volumes in pure CO2 proceeds smoothly, it may be possible to begin gathering kinetic data for the PTAD/anthracene system in cosolvent modified CO_2. A set of scouting experiments will be designed to select among candidate cosolvents for those which provide optimum enhancement of PTAD/anthracene reaction kinetics.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^S}{V^S}\right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P}\right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T}\right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

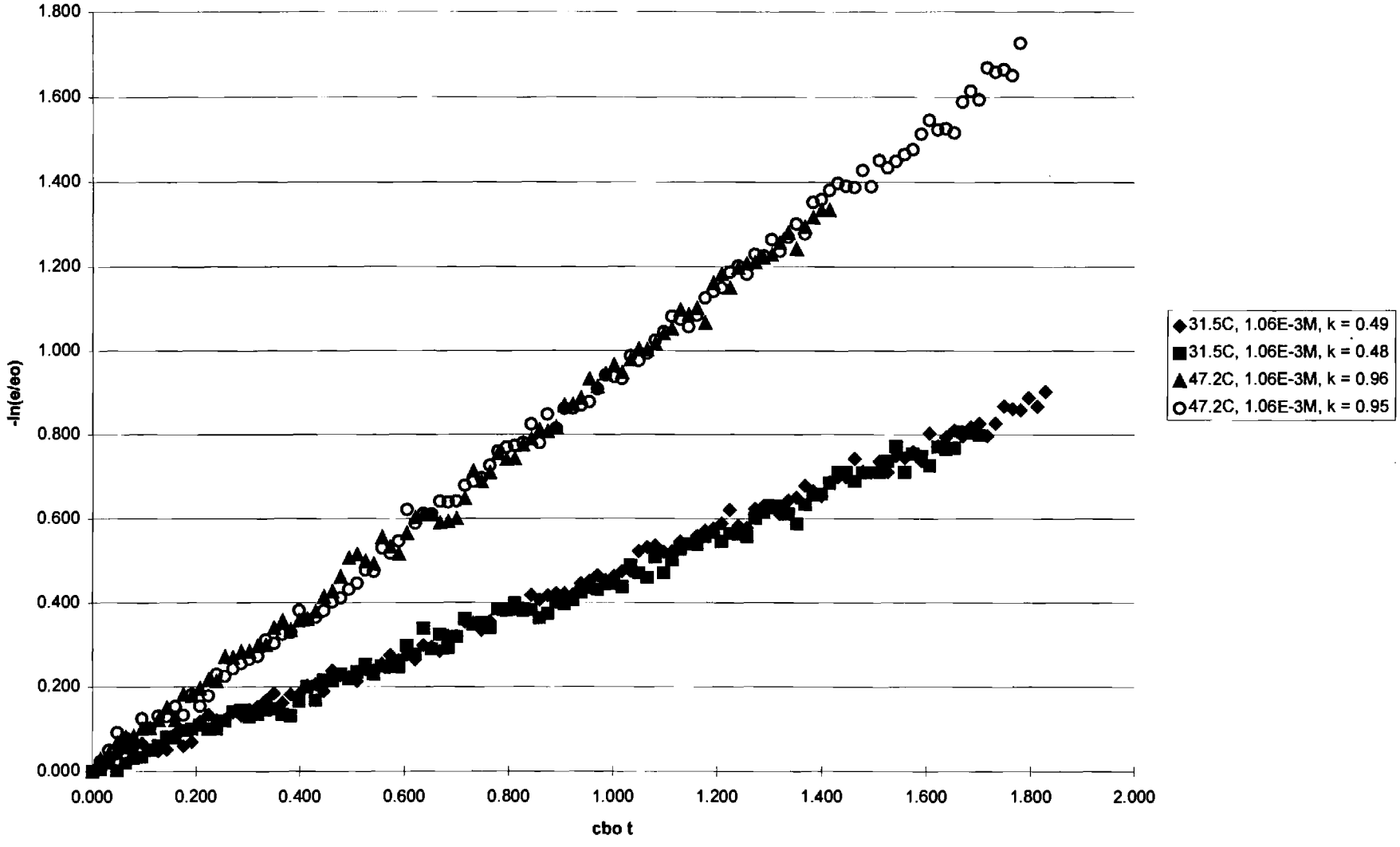
Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

SUMMARY

We have completed the liquid phase work of the reaction of several dienophiles with anthracene in acetonitrile. Our fluorescence spectroscopic techniques were used to obtain the kinetic data for PTAD with anthracene, and the values obtained for observed first order rate constant closely match those reported by A. I. Konvalov (1979). We have constructed equipment necessary for the measurement of the solubility of PTAD in supercritical CO2, and have completed calibration of the equipment. Solubility measurements will be made during the coming quarter. When the solubility measurements have been completed, the collection of kinetic data for the PTAD/anthracene system in supercritical CO2 will begin in earnest. It is reasonable to expect that at least one isotherm of kinetic data can be completed during this quarter.

Appendix

Figure 1. PTAD w/ Anthracene in Liquid Acetonitrile
k=.35 1/Ms at 25C, +/-4%



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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 894-7070

Initiation Date: September 1, 1994

Period Covered by Report: October 1, 1995 - December 31, 1995

ABSTRACT

The solubility of the nitrogen bearing dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) has been measured as a function of pressure at 40 C, with the exception of points at 2500 psig and 3000 psig. When collection of these last points has been accomplished, the collection of all preliminary data needed to begin kinetic studies of the Diels-Alder reaction between PTAD and anthracene at 40 C in supercritical CO_2 will be complete.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

PROGRESS THIS QUARTER

COLLECTION OF SOLUBILITY DATA

The solubility of PTAD in pure CO2 at 40 C is nearing completion. The data set as it currently exists is presented in the Appendix as Figure 1. Additional points will be taken at 2500 psig, and at 3000 psig.

As mentioned in a previous report, some preliminary measurements of the kinetics of anthracene and PTAD in supercritical CO2 have been completed. Results confirmed that this reaction does run in the supercritical phase, and that the reaction has a conveniently short half-life, but that the solubility of PTAD in supercritical CO2 is low. This low solubility necessitated the acquisition of accurate solubility data for the temperatures and pressures at which the reaction will be run. PTAD must be introduced into the reaction cell in quantities below its solubility limit in order to avoid the distortion of results that would occur if the experiments were performed with excess solid PTAD in the bottom of the reaction cell. Obviously, the concentration of the excess reactant PTAD must be known accurately in order to obtain the true rate constant from data in which a pseudo first order rate constant was measured. In order for the concentration of the PTAD to be accurately known, all PTAD introduced into the reaction volume must be present in the fluid phase.

Another more subtle distortion of kinetics in the presence of excess solid PTAD would occur with the reaction of anthracene with PTAD at the solid-fluid interface. In this case, the disappearance of anthracene - which produces the measured signal in fluorescence spectroscopy - would proceed by a complex mechanism involving both supercritcal phase kinetics and solid kinetics. This event would have the effect of distorting the measured value of the observed pseudo first order rate constant.

PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

We shall begin collection of kinetic data for the system of PTAD with anthracene in supercritical CO_2 at 40 C. Kinetic data will be collected at various pressures along the 40 C isotherm, and will be correlated with respect to the following equation:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -\frac{\Delta v^{\ddagger}}{RT}$$

Scouting experiments have been designed which will select among candidate cosolvents for those which provide optimum enhancement of PTAD/anthracene reaction kinetics. These scouting experiments will be run.

THERMODYNAMIC MEASUREMENTS

A recently developed technique uses a supercritical fluid chromatograph for the rapid and facile measurement of the fugacity of dilute solutes in SCF's [Ekart, 1993], which is a variation on several previous successful techniques [Smith, 1987; Bartle, 1990; Bartle, 1990; Shim, 1991]. The chromatograph equilibrates a dilute solute between the stationary phase and a mobile (supercritical fluid) phase. The retention time, t, of solute i defines the capacity factor, k_i

$$k_i = \frac{t_i - t_o}{t_o} \tag{3}$$

Equation (4) gives the infinite dilution fugacity coefficient, ϕ_i^∞, in terms of the capacity factor and column dependent factors.

$$\phi_i^\infty = \frac{k_i H_i}{P v^F} \left(\frac{V^F v^S}{V^S}\right) \tag{4}$$

H_i is the Henry's law constant for the solute and the stationary phase, V is the total volume, v is the molar volume and F & S represent the fluid and the stationary phases, respectively.

The pressure and temperature derivatives of the fugacity coefficient, give the partial molar volume, v_i^∞, and partial molar enthalpy, h_i^∞, Equations (5) and (6).

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial P}\right)_T = v_i^\infty \tag{5}$$

$$RT\left(\frac{\partial \ln \phi_i^\infty}{\partial T}\right)_P = -\frac{h_i^\infty}{T} \tag{6}$$

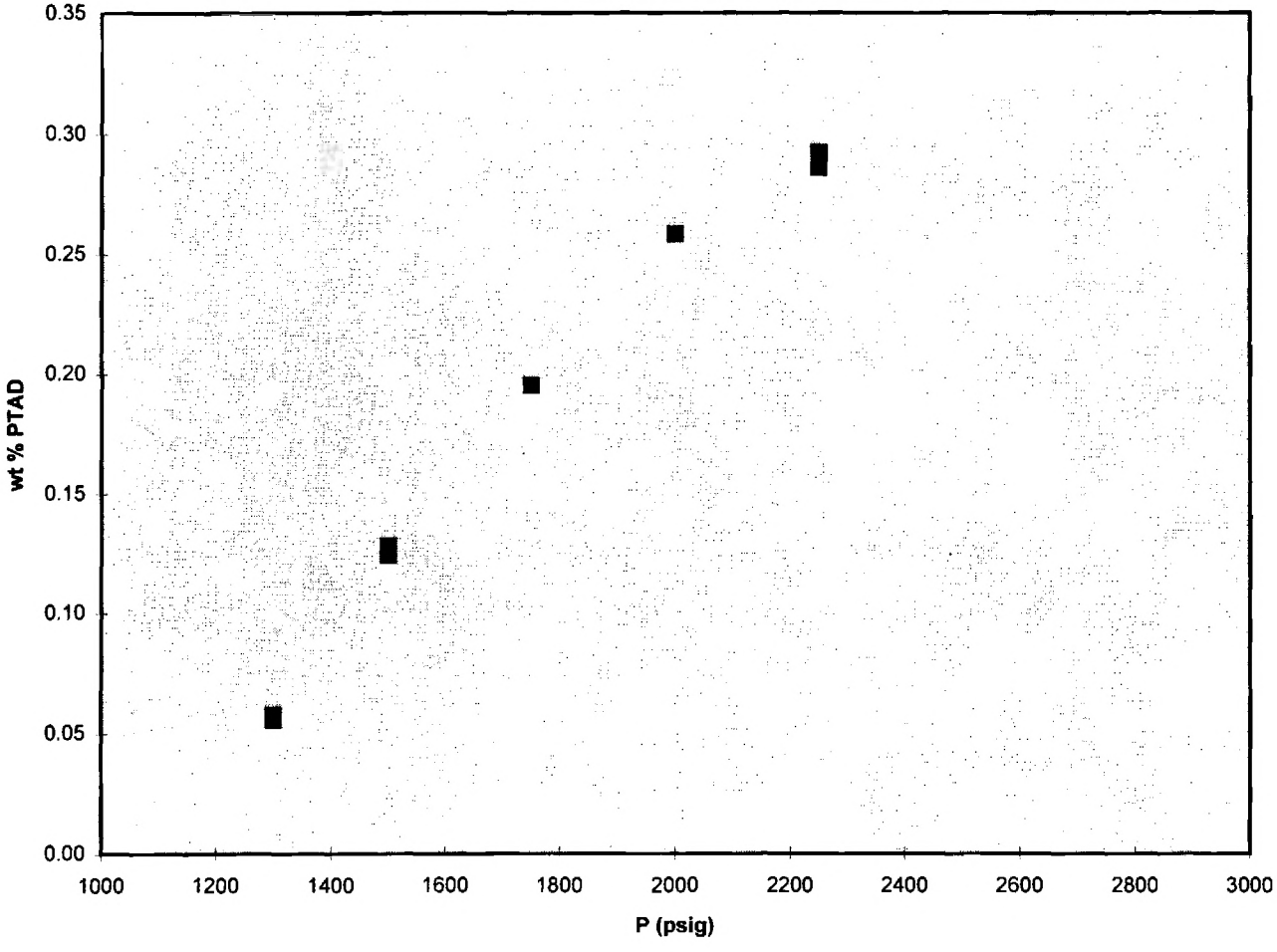
Combining Equations (5) & (6) with Equation (4) allow the partial molar properties to be determined with retention time data only.

SUMMARY

Acquisition of the data needed for kinetic studies of the Diels-Alder reaction of PTAD with anthracene in pure CO_2 at 40 C is nearly complete. When the solubility measurements have been completed, the collection of kinetic data for the PTAD/anthracene system in supercritical CO2 will begin. It is reasonable to expect that at least one isotherm of kinetic data can be completed during this quarter.

Appendix

Figure 1. Solubility of PTAD in Pure CO2 at 40 C



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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School Chemical Engineering & Specialty Separations Center
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Initiation Date: September 1, 1994

Period Covered by Report: January 1, 1996 - March 31, 1996

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The tautomeric equilibrium of a Schiff base was chosen as the model system and was investigated in supercritical ethane and cosolvent modified supercritical ethane.

OBJECTIVES

The goal of this work is to develop benign solvent/cosolvent systems for reactions which will achieve optimum denitrogenation in the pretreatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density, which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [1-3], as well as in many specific applications to environmental control [4,5].

The objectives of this work are: utilize supercritical fluids and modified supercritical fluids to tune the chemical equilibria of model coal compounds; and, model the density dependence of the equilibrium constant using a chemical-physical approach. This approach allows us to ascertain the contributions of hydrogen bonding of cosolvents, and the density augmentation to the changes in equilibrium constant. By understanding the effects of these contributions to the equilibrium constant we will be able to quantitatively tune reaction equilibria in supercritical fluids.

PROGRESS THIS QUARTER

Cosolvent Mixture Density Measurements

The density of pure ethane was measured to verify the reliability of the experimental procedure used in this study. A comparison of the measured ethane densities, at various pressures, and the literature values [6] is given in Figure 1; all the measured data are in good agreement with the literature values, less than ±0.5% deviation for $P > 55$ bar and ±3.3% for $P < 55$ bar, the literature data have uncertainties of ±0.2% away from the critical region and ±5% in the critical region. This set of data has been duplicated and shown to be reproducible. The deviation between the measured and literature data for pure ethane density provides a good estimate of the uncertainty associated with the experimental procedure.

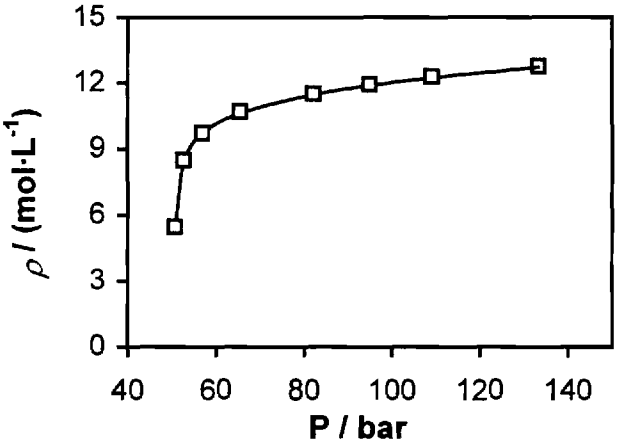


Figure 1. Density of Pure Ethane at 308.2 K (experimental, — literature data)

Mixture densities are compared with pure ethane densities in Table 1. At low cosolvent concentrations, mixture densities are close to the pure solvent densities in the higher pressure region, but deviate significantly in the highly compressible region. Hence, the usual assumption that the density of supercritical solvent + cosolvent mixtures may be approximated by that of the pure solvent may result in serious error, even at very low cosolvent concentration.

Table 1. Densities of binary supercritical ethane + cosolvent mixtures at 308.2 K ethane (A) + 1,1,1,3,3,3-hexafluoro-2-propanol (B)

x_B = 0.0068					x_B = 0.0136			
P/bar	$\rho_{mixture}$/ (mol/L)	ρ_{pure}[a]/ (mol/L)	%Dev.[b]		P/bar	$\rho_{mixture}$/ (mol/L)	ρ_{pure}[a]/ (mol/L)	%Dev.[b]
102.3	11.97	12.08	-0.9		103.3	12.04	12.10	-0.5
84.6	11.49	11.55	-0.5		87.7	11.64	11.66	-0.2
76.8	11.20	11.24	-0.4		76.4	11.25	11.23	0.18
69.5	10.86	10.88	-0.2		68.0	10.86	10.78	0.7
62.5	10.41	10.37	0.4		61.7	10.47	10.29	1.8
57.1	9.87	9.72	1.5		56.4	9.99	9.61	4.0
53.7	9.28	8.87	4.6		54.7	9.76	9.22	5.9
52.0	8.76	7.60	15.3		52.2	9.28	7.88	17.8
51.3	8.31	6.29	32.1		51.1	8.89	5.78	53.8
50.7	7.62	5.31	43.5					
50.5	7.09	5.09	39.3					

Table 2 (cont.)
ethane (A) + 2,2,2-trifluoroethanol (B)

x_B = 0.0098					x_B = 0.0198			
P/bar	$\rho_{mixture}$/ (mol/L)	ρ_{pure}[a]/ (mol/L)	%Dev.[b]		P/bar	$\rho_{mixture}$/ (mol/L)	ρ_{pure}[a]/ (mol/L)	%Dev.[b]
103.2	12.07	12.10	-0.2		102.6	11.97	12.09	-1.0
84.2	11.55	11.54	0.1		84.6	11.50	11.55	-0.4
76.9	11.27	11.25	0.2		76.9	11.23	11.24	-0.1
69.9	10.95	10.90	0.5		69.9	10.94	10.90	0.4
63.3	10.55	10.44	1.1		62.9	10.54	10.40	1.3
57.5	10.00	9.79	2.1		57.0	10.04	9.71	3.4
54.1	9.47	9.03	4.9		53.8	9.59	8.90	7.8
52.5	9.03	8.17	10.5		51.9	9.22	7.38	24.9
51.4	8.48	6.43	32.0		50.7	8.67	5.23	65.8
50.7	7.51	5.23	43.6		49.8	8.11	4.59	76.7
50.4	6.70	4.97	34.8					

Table 2 (cont.)
ethane (A) + ethanol (B)

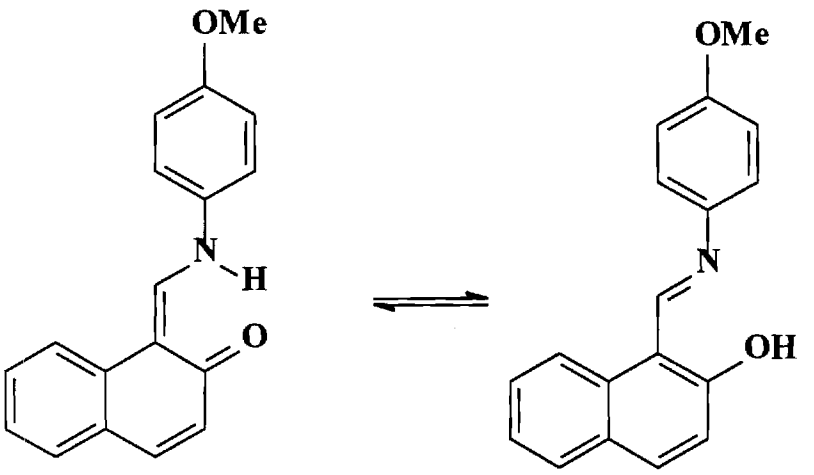
x_B = 0.0168			
P/bar	$\rho_{mixture}$/ (mol/L)	ρ_{pure}[a]/ (mol/L)	%Dev.[b]
105.7	12.27	12.16	0.9
84.2	11.72	11.54	1.6
76.5	11.45	11.23	2.0
69.8	11.17	10.89	2.6
62.7	10.78	10.38	3.9
56.3	10.26	9.57	7.2
53.4	9.91	8.81	12.5
51.9	9.60	7.38	30.1
50.6	9.18	5.16	77.9
49.7	8.72	4.51	93.3

a Younglove, B.A. and Ely, J.F., 1987.
b %Dev. = $(\rho_{mixture} - \rho_{pure})x100/\rho_{pure}$

Keto-Enol Equilibrium Measurements

Recent studies of chemical equilibria have focused on the effects of pressure on the equilibrium constants of solutes in pure supercritical fluids [7-9]. The presence of a cosolvent complicates the system, especially if the cosolvent is capable of participating in specific interactions with the solute molecule and leads to a multiple equilibria. However, it is the purpose of this study to quantify the effect of cosolvents on keto-enol

equilibrium constant for the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol (Figure 2), especially in the near-critical region where local composition enhancements are expected to have a large effect on the equilibrium constant.



KETO **ENOL**

Figure 2. Tautomeric equilibrium of the Schiff base 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol.

The Schiff base and a blocked Schiff base (Figure 3) were synthesized by a condensation reaction of 2-hydroxynaphthaldehyde and p-methoxy aniline in ethanol[10] and by a condensation reaction of 2-methoxy-1-naphthaldehyde and 4-methoxyaniline in ethanol, respectively. Yellow solids of blocked Schiff base were obtained after filtration, washing twice with cold ethanol and drying under vacuum. ^{1}H NMR ($CDCL_3$ and TMS): δ = 3.78 ppm (s, 3H); 6.94 ppm (d, 2H); 7.18 ppm (d, 1H); 7.30 ppm (d, 2H); 7.36 ppm (m, 1H); 7.56 ppm (m, 1H); 7.74 ppm (d,1H); 7.85 ppm (d, 1H); 9.25 ppm (s, 1H); 9.53 ppm (d, 1H); 13C NMR ($CDCl_3$ and TMS): δ = 55.30 ppm (s); 56.26 ppm (s); 112.53 ppm (s); 114.38 ppm (s); 117.37 ppm (s); 122.30 ppm (s); 124.23 ppm (s); 126.07 ppm (s); 128.29 ppm (s); 128.40 ppm (s); 129.26 ppm (s); 132.05 ppm (s); 133.39 ppm (s); 146.61 ppm (s); 157.02 ppm (s); 158.22 ppm (s); 159.31 ppm (s). The blocked Schiff base had the phenolic oxygen methylated to prohibit tautomerization so that the extinction coefficients of the enol form of the Schiff could be measured.

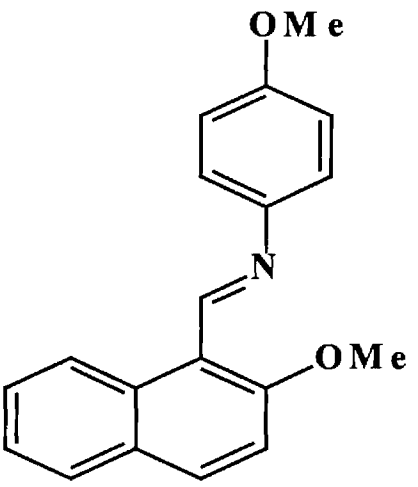


Figure 3. Blocked Schiff base.

Apparatus

A schematic of the modified UV spectrophotometer (Perkin Elmer 554) is shown in Figure 4. Single beam spectroscopy was used in this double beam apparatus using air as a constant background for enhanced signal to noise ratio. The spectrophotometer was modified to accommodate a stainless steel high pressure cell[11] with quartz windows (Heraeus Amersil). The path length of the cell was 0.75 cm and the volume was 5.88 ml. The cell was stirred continuously using a mini stir plate (Variomag) and a stir bar (Fisher) placed inside the cell.

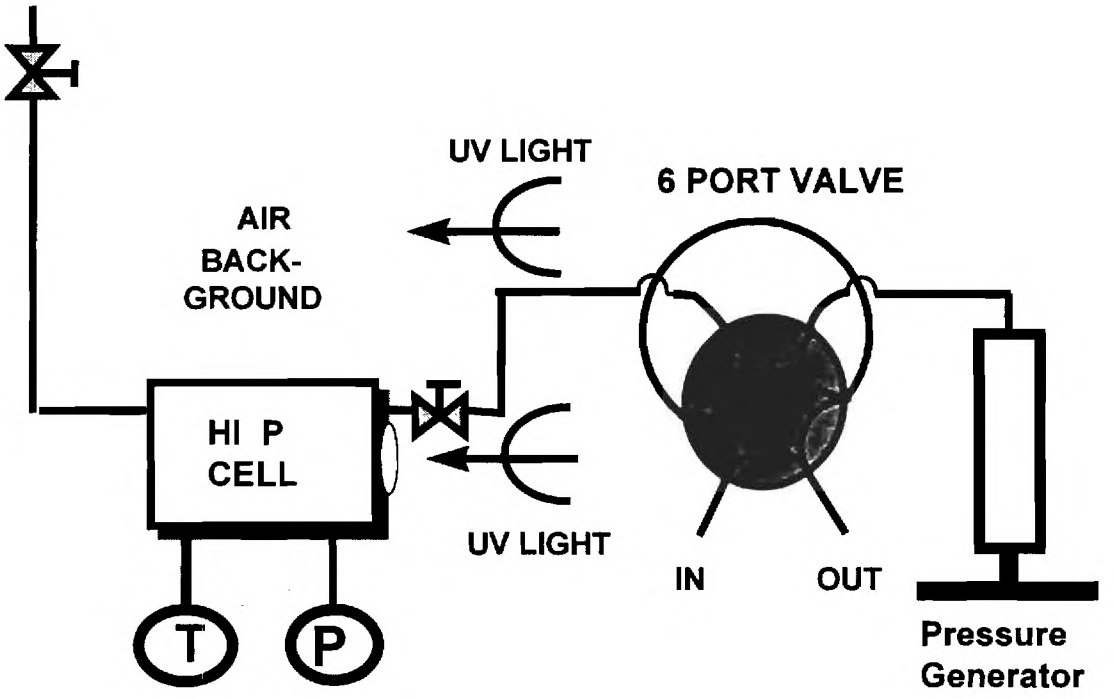


Figure 4. Schematic diagram of high pressure UV-Vis reaction apparatus.

The temperature inside the cell was monitored with an internal thermistor (Omega, calibrated within ± 0.1°C) and controlled manually using an EPSCO DC power supply (Model D-612T). Heat was supplied by thermoelectric heaters (Melcor). The pressure was controlled using a 60 cm^3 piston type high pressure generator (High Pressure Equipment, Model 87-6-5) and measured to within ± 2 psi with a Heise digital pressure gauge (Model 901B). A Valco 6-port sampling valve with external sample loops ranging in size from 20-100μl was used to inject cosolvent directly into the high pressure cell.

Procedure

Single beam spectroscopy was used to monitor absorbance as a function of increasing pressure at constant probe and cosolvent concentrations. All measurements were made at a constant temperature of 35°C (± 0.1°C), and all experiments were carried out in the single phase region, as confirmed by separate miscibility experiments [12] (Table 3).

Table 3. Pressure limits of miscibility for SCF ethane/cosolvent mixtures.

Cosolvent in SCF Ethane	Cosolvent Concentration (mol/L)	Lower Miscibility Limit (psig)
Trifluoroethanol	0.24	800
Trifluoroethanol	0.12	756
Trifluoroethanol	0.046	738
Hexafluoroiso-propanol	0.32	721
Hexafluoroiso-propanol	0.16	713
Hexafluoroiso-propanol	0.08	Miscible at all conditions observed.
Ethanol	0.2	Miscible at all conditions observed.
Ethanol	0.1	Miscible at all conditions observed.

Spectra at different pressures were recorded, starting with a low pressure as determined by the miscibility limit, and incrementally going to higher pressures. The absorbance was recorded at the wavelength of maximum absorption for each tautomer at least three times to obtain an average value (standard error ± 2% at higher pressures; ± 5% at pressures below 730 psig). The pressure varied less than 1.5 psi within a single spectral scan, and data were taken with increasing pressure to ensure that the solute concentration remained constant. Since single beam spectroscopy was used in this double beam apparatus, blank runs (no Schiff base) were made for each solvent system at every pressure point, and this subsequent spectrum was subtracted from the spectrum which contained the Schiff base.

The high-pressure cell was loaded with a solution of 20 μl of (0.0437 M) Schiff base in acetone using a syringe to obtain a probe concentration of 1.5×10^{-4} M, which is below the solubility limit at experimental conditions as determined spectroscopically. The cell was flushed with multiple volumes of low pressure ethane to evaporate the acetone and to displace air from the system. In the experiments without cosolvent, the cell was then pressurized with ethane to the desired initial pressure. In cases where cosolvent was added, the cell was charged with 100 psig of ethane after removing air from the system. Then, the cell was isolated from the rest of the system, and the lines leading to the cell were pressurized with 450 psig of ethane. The external sample loop was then rinsed and filled with the cosolvent, and the sampling valve and the valve leading to the cell were opened simultaneously to force the cosolvent into the cell using the pressure differential. The cell was further pressurized with ethane to the desired pressure set point, and after equilibration of temperature and pressure, absorbance spectra were measured as described above.

Calculation of K_C

The equilibrium constant (K_C) was calculated from the following equation:

$$K_c = \frac{c_{keto}}{c_{enol}} \tag{1}$$

where c_{keto} is the concentration of the keto tautomer and c_{enol} is the concentration of the enol tautomer. Concentration is related to the measured absorbance through Beer's law, thus,

$$K_C = \left(\frac{\varepsilon_{enol}}{\varepsilon_{keto}}\right)\left(\frac{A_{\lambda \max,keto}}{A_{\lambda \max,enol}}\right) \tag{2}$$

where A represents the absorbance at the maximum wavelength for each tautomer for a given solvent system. The ratio of extinction coefficients and absorbances were obtained as described previously. The wavelength of maximum absorption changes for the various cosolvent modified SCF solutions due to solvochromatic shifts.

RESULTS & DISCUSSION

The equilibrium constant was measured as a function of density in supercritical ethane modified with three different concentrations of hexafluoroisopropanol (HFIP). Figure 5 summarizes the results.

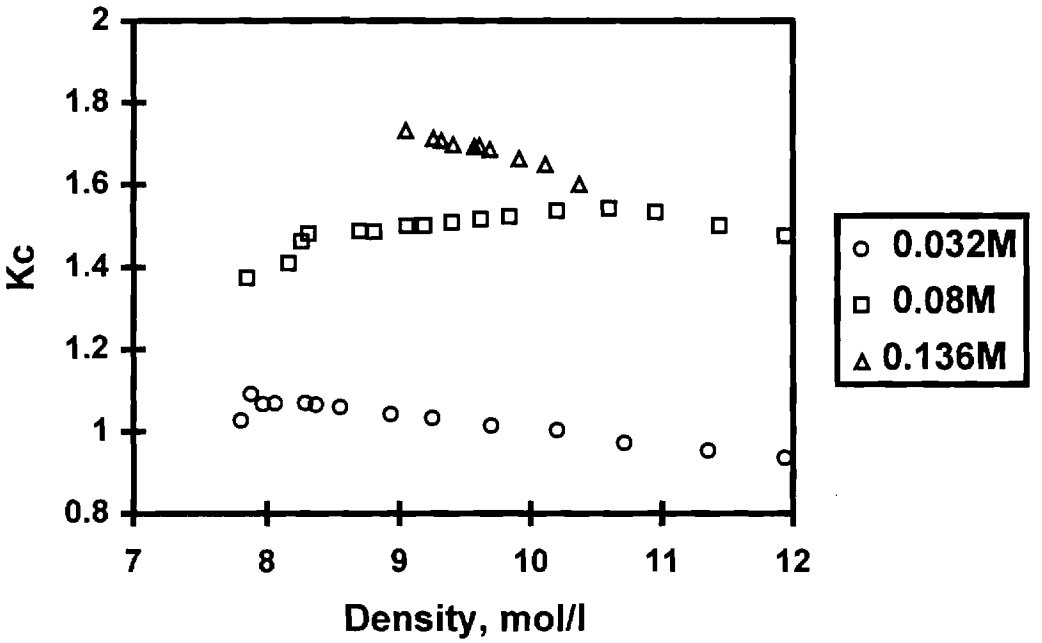


Figure 5. Density dependence of the tautomeric equilibrium constant in supercritical ethane modified with hexafluoroisopropanol at 35C. Cosolvent concentration is the parameter

Clearly, the equilibrium constant increases with increasing HFIP concentration. As the cosolvent concentration increases the degree of hydrogen bonding increases also which in turns leads to an increase in the tautomeric equilibrium constant.

PLANS FOR NEXT QUARTER

The tautomeric equilibrium constant for the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol will be measured in supercritical ethane modified with trifluoroethanol (TFE) and ethanol at various concentrations in the near critical region.

The density dependence of the tautomeric equilibrium constant will be modeled using a chemical-physical approach. The following dialogue summarizes our modeling approach. Possible relationships describing these equilibria in a cosolvent modified solvent system are shown below. The equilibrium constant K_1 is the actual tautomerization between the keto and enol forms of the Schiff base. The equilibrium constants K_2 and K_3 indicate the equilibrium between the cosolvent, a hydrogen bond donor, and the Schiff base tautomers which are hydrogen bond acceptors, along with the

hydrogen bonded complex of each form. Finally K_4 is the equilibrium constant for the dimerization of the alcohol cosolvents. Other equilibria such as the formation of higher self-associates of the alcohol cosolvents are neglected. In addition, HFIP exists in an equilibrium between two rotamer forms which have slightly different acidities. This equilibrium is know to vary with density[13], however, should have negligible effects on the Schiff tautomerization and will be ignored.

$$\begin{aligned} K &\overset{K_1}{\leftrightarrow} E \\ K + H &\overset{K_2}{\leftrightarrow} KH \\ E + H &\overset{K_3}{\leftrightarrow} EH \\ H + H &\overset{K_4}{\leftrightarrow} HH \end{aligned} \qquad (3)$$

Where K , E, and H designate the keto tautomer, enol tautomer, and cosolvent, respectively.

For simplification, only cosolvent systems with minimal self-association will be modeled. The self association of fluorinated alcohols such as TFE is minimal, and with HFIP, there is essentially no dimerization at the concentrations used[8,14,15]. Additionally, it was found from gas phase hydrogen bonding data between the fluoro-alcohols and various ketonic and enolic (phenolic, in particular, such as the enol form of the Schiff base used in this investigation) compounds that the third equilibrium (K_3) may be ignored [14,16] because the equilibrium constant for hydrogen bonds between fluoro-alcohols and ketones is so much greater in comparison to that between the fluoro-alcohols and the phenolic compounds. This results in a model based on only two equilibrium constants:

$$K_1 = \frac{z_K \phi_K}{z_E \phi_E} \qquad (4)$$

$$K_2 = \frac{z_{KH} \phi_{KH}}{z_K \phi_K z_H \phi_H} \qquad (5)$$

where z_K, z_E, and z_{KH} are the true concentrations of the keto and enol tautomers of the Schiff base, respectively, and the keto hydrogen bonded complex; and the ϕ_K, ϕ_E, and ϕ_{KH} are the fugacity coefficients for these species.

In order to compare the model directly to the experimental results, an expression in terms of the experimental equilibrium constant was derived. For this derivation, it was assumed that the fugacity coefficients for each of the free Schiff tautomers (ϕ_K and ϕ_E) were equal and the free cosolvent concentration was constant, because in all cases the added

cosolvent was in great excess of the Schiff base concentration. Then, the experimental equilibrium constant is given by,

$$K_{C,\exp} = \frac{\left[c_K + c_{KH}\right]}{\left[c_E\right]} \tag{6}$$

where the concentration of the keto tautomer is now a combination of the free and hydrogen bonded form of the tautomer. Then, the equilibrium constant calculated from a physical-chemical analysis becomes,

$$K_{C,calc} = K_1(1 + K_2 C_{\cos}\phi^*) \tag{7}$$

where

$$\phi^* = \frac{\phi_K \phi_H}{\phi_{KH}}, \tag{8}$$

K_1, K_2 are defined previously in equations 4 and 5, and C_{cos} is the bulk cosolvent concentration.

The fugacity coefficients will be calculated from the Peng-Robinson equation of state[17]. The critical properties of ethane, ethanol[17], and TFE[18] may be obtained from the literature. The critical temperatures of HFIP, Schiff base, and Schiff base/cosolvent hydrogen bonded complex can be estimated from Fedors method; the critical pressure and volume for the same compounds will be estimated using the Joback method; and the acentric factor estimated from the critical volume[17].

SUMMARY

Densities of binary supercritical mixtures of ethane with cosolvents, ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, have been measured by a constant volume apparatus. Measurements were made in the range 0.7 to 2.0 mol % cosolvent and pressure from 49.8 to 105.7 bar at 308.2 K. The tautomeric equilibrium constant was measured as a function of density in supercritical ethane modified with three different concentrations of hexafluoroisopropanol (HFIP). The measured equilibrium constant was found to be a function of fluid density and cosolvent concentration.

Future work will investigate the effect of different cosolvents. Modeling of the results will commence using a chemical-physical approach.

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering & Specialty Separations Center
(404) 894-7070

Initiation Date: September 1, 1994

Period Covered by Report: April 1, 1996 - June 30, 1996

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The tautomeric equilibrium of a Schiff base was chosen as the model system and was investigated in supercritical ethane and cosolvent modified supercritical ethane.

OBJECTIVES

The goal of this work is to develop benign solvent/cosolvent systems for reactions which will achieve optimum denitrogenation in the pretreatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density, which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general (Johnston, 1989; Ely, 1991; Brennecke, 1989), as well as in many specific applications to environmental control (Leman, 1990; Eckert, 1986).

The objectives of this work are: utilize supercritical fluids and modified supercritical fluids to tune the chemical equilibria of model coal compounds; and, model the density dependence of the equilibrium constant using a chemical-physical approach. This approach allows us to ascertain the contributions of hydrogen bonding of cosolvents, and the density augmentation to the changes in equilibrium constant. By understanding the effects of these contributions to the equilibrium constant we will be able to quantitatively tune reaction equilibria in supercritical fluids.

PROGRESS THIS QUARTER

Keto-Enol Equilibrium Measurements

Recent studies of chemical equilibria have focused on the effects of pressure on the equilibrium constants of solutes in pure supercritical fluids (Yagi, 1993; Kazarian, 1993; Yamasaki, 1990). The presence of a cosolvent complicates the system, especially if the cosolvent is capable of participating in specific interactions with the solute molecule and leads to multiple equilibria. However, it is the purpose of this study to quantify the effect of cosolvents on keto-enol equilibrium constant for the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol (Figure 1), especially in the near-critical region where local composition enhancements are expected to have a large effect on the equilibrium constant.

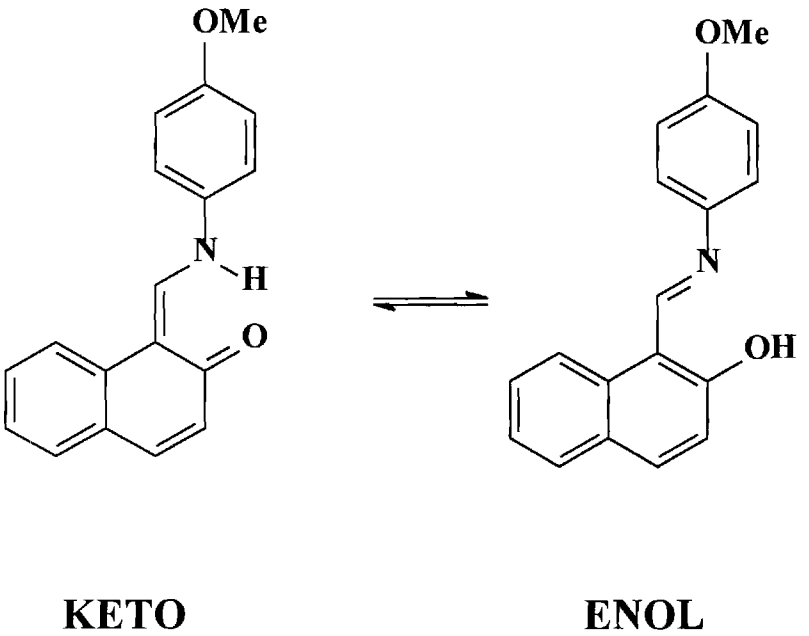

Figure 1. Tautomeric equilibrium of the Schiff base 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol.

The Schiff base and a blocked Schiff base (Figure 2) were synthesized by a condensation reaction of 2-hydroxynaphthaldehyde and p-methoxy aniline in ethanol (Salman, 1991) and by a condensation reaction of 2-methoxy-1-naphthaldehyde and 4-methoxyaniline in ethanol, respectively. Yellow solids of blocked Schiff base were obtained after filtration, washing twice with cold ethanol and drying under vacuum. ^{1}H NMR ($CDCL_3$ and TMS): δ = 3.78 ppm (s, 3H); 6.94 ppm (d, 2H); 7.18 ppm (d, 1H); 7.30 ppm (d, 2H); 7.36 ppm (m, 1H); 7.56 ppm (m, 1H); 7.74 ppm (d,1H); 7.85 ppm (d, 1H); 9.25 ppm (s, 1H); 9.53 ppm (d, 1H); 13C NMR ($CDCl_3$ and TMS): δ = 55.30 ppm (s); 56.26 ppm (s); 112.53

ppm (s); 114.38 ppm (s); 117.37 ppm (s); 122.30 ppm (s); 124.23 ppm (s); 126.07 ppm (s); 128.29 ppm (s); 128.40 ppm (s); 129.26 ppm (s); 132.05 ppm (s); 133.39 ppm (s); 146.61 ppm (s); 157.02 ppm (s); 158.22 ppm (s); 159.31 ppm (s). The blocked Schiff base had the phenolic oxygen methylated to prohibit tautomerization so that the extinction coefficients of the enol form of the Schiff could be measured.

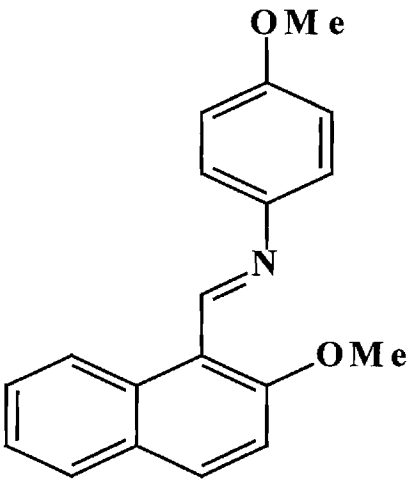

Figure 2. Blocked Schiff base.

Apparatus

A schematic of the modified UV spectrophotometer (Perkin Elmer 554) is shown in Figure 3. Single beam spectroscopy was used in this double beam apparatus using air as a constant background for enhanced signal to noise ratio. The spectrophotometer was modified to accommodate a stainless steel high pressure cell (Tomasko, 1992) with quartz windows (Heraeus Amersil). The path length of the cell was 0.75 cm and the volume was 5.88 ml. The cell was stirred continuously using a mini stir plate (Variomag) and a stir bar (Fisher) placed inside the cell.

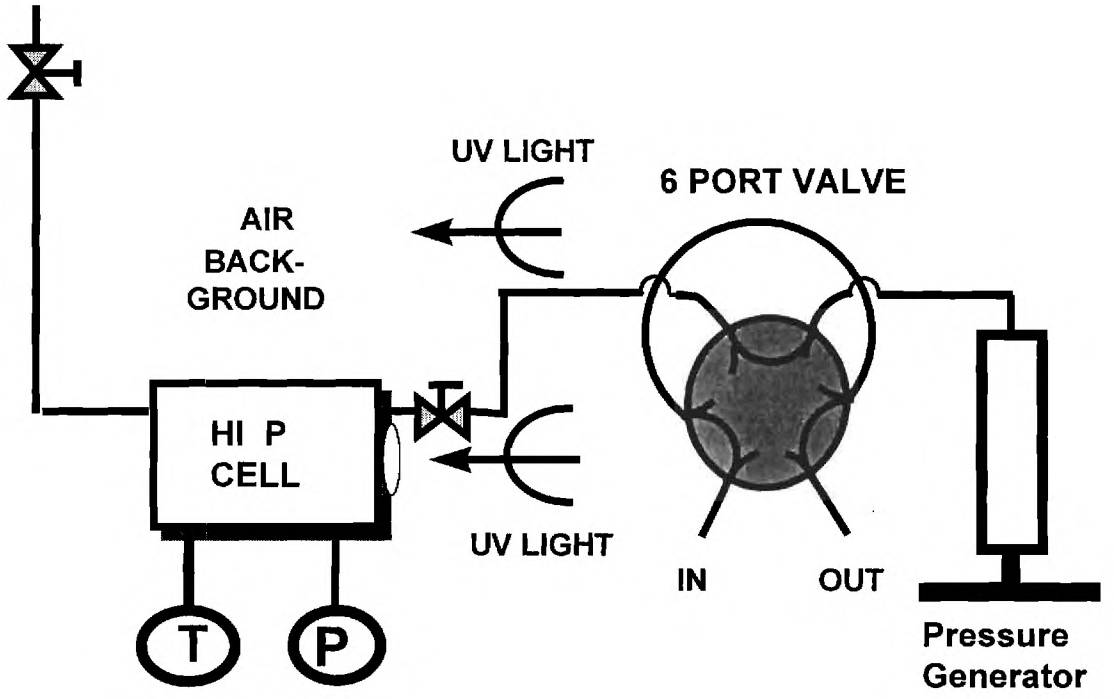

Figure 3. Schematic diagram of high pressure UV-Vis reaction apparatus.

The temperature inside the cell was monitored with an internal thermistor (Omega, calibrated within ± 0.1°C) and controlled manually using an EPSCO DC power supply (Model D-612T). Heat was supplied by thermoelectric heaters (Melcor). The pressure was controlled using a 60 cm^3 piston type high pressure generator (High Pressure Equipment, Model 87-6-5) and measured to within ± 2 psi with a Heise digital pressure gauge (Model 901B). A Valco 6-port sampling valve with external sample loops ranging in size from 20-100μl was used to inject cosolvent directly into the high pressure cell.

Procedure

Single beam spectroscopy was used to monitor absorbance as a function of increasing pressure at constant probe and cosolvent concentrations. All measurements were made at a constant temperature of 35°C (± 0.1°C), and all experiments were carried out in the single phase region, as confirmed by separate miscibility experiments (Yun, Accepted April 1996) (Table 1).

Table 1. Pressure limits of miscibility for SCF ethane/cosolvent mixtures.

Cosolvent in SCF Ethane	Cosolvent Concentration (mol/L)	Lower Miscibility Limit (psig)
Trifluoroethanol	0.24	800
Trifluoroethanol	0.12	756
Trifluoroethanol	0.046	738
Hexafluoroiso-propanol	0.32	721
Hexafluoroiso-propanol	0.16	713
Hexafluoroiso-propanol	0.08	Miscible at all conditions observed.
Ethanol	0.2	Miscible at all conditions observed.
Ethanol	0.1	Miscible at all conditions observed.

Spectra at different pressures were recorded, starting with a low pressure as determined by the miscibility limit, and incrementally going to higher pressures. The absorbance was recorded at the wavelength of maximum absorption for each tautomer at least three times to obtain an average value (standard error ± 2% at higher pressures; ± 5% at pressures below 730 psig). The pressure varied less than 1.5 psi within a single spectral scan, and data were taken with increasing pressure to ensure that the solute concentration remained constant. Since single beam spectroscopy was used in this double beam apparatus, blank runs (no Schiff base) were made for each solvent system at every pressure point, and this subsequent spectrum was subtracted from the spectrum which contained the Schiff base.

The high-pressure cell was loaded with a solution of 20 µl of (0.0437 M) Schiff base in acetone using a syringe to obtain a probe concentration of 1.5×10^{-4} M, which is below the solubility limit at experimental conditions as determined spectroscopically. The cell was flushed with multiple volumes of low pressure ethane to evaporate the acetone and to displace air from the system. In the experiments without cosolvent, the cell was then pressurized with ethane to the desired initial pressure. In cases where cosolvent was added, the cell was charged with 100 psig of ethane after removing air from the system. Then, the cell was isolated from the rest of the system, and the lines leading to the cell were pressurized with 450 psig of ethane. The external sample loop was then rinsed and filled with the cosolvent, and the sampling valve and the valve leading to the cell were opened simultaneously to force the cosolvent into the cell using the pressure differential. The cell was further pressurized with ethane to the desired pressure set point, and after equilibration of temperature and pressure, absorbance spectra were measured as described above.

Calculation of K_C

The equilibrium constant (K_C) was calculated from the following equation:

$$K_c = \frac{c_{keto}}{c_{enol}} \tag{1}$$

where c_{keto} is the concentration of the keto tautomer and c_{enol} is the concentration of the enol tautomer. Concentration is related to the measured absorbance through Beer's law, thus,

$$K_c = \left(\frac{\varepsilon_{enol}}{\varepsilon_{keto}}\right)\left(\frac{A_{\lambda \max,keto}}{A_{\lambda \max,enol}}\right) \tag{2}$$

where A represents the absorbance at the maximum wavelength for each tautomer for a given solvent system. The ratio of extinction coefficients and absorbances were obtained as described previously. The wavelength of maximum absorption changes for the various cosolvent modified SCF solutions due to solvochromatic shifts.

Results and Discussion

The experimental equilibrium constant was found to be a function of cosolvent acidity, cosolvent concentration, and density. Polar cosolvents such as acetone, chloroform, and dimethylacetamide (DMA) did not affect the position of tautomeric equilibria. Only cosolvents capable of hydrogen bonding (EtOH, TFE, and HFIP) led to any significant amount of Schiff base tautomerization; the equilibrium constant shifted towards the keto tautomer in the presence of cosolvents which were capable of forming hydrogen bonds. The equilibrium constant also increased with increasing acidity of the cosolvent as can be seen in Figure 4.

The equilibrium constant was also found to shift substantially with varying amounts of cosolvents as can be seen in Figure 5 with the TFE modified SCF ethane solvent system.

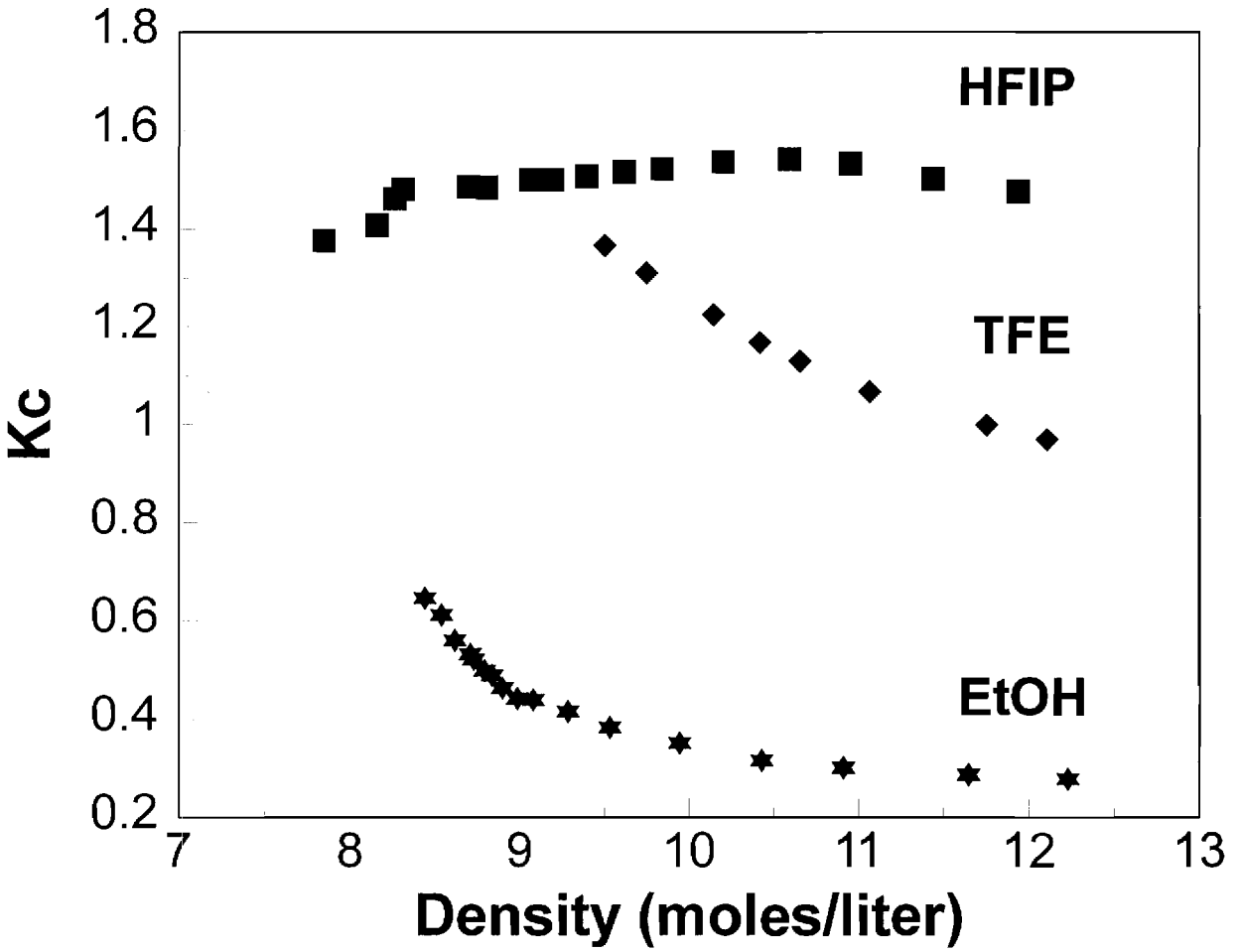

Figure 4. Equilibrium constant (K_c) as a function of density for approximately 0.1 M cosolvent (EtOH, TFE, HFIP) in SCF ethane. (Equilibrium constant (K_c) as a function of density for approximately 0.1 M cosolvent in SCF ethane.)

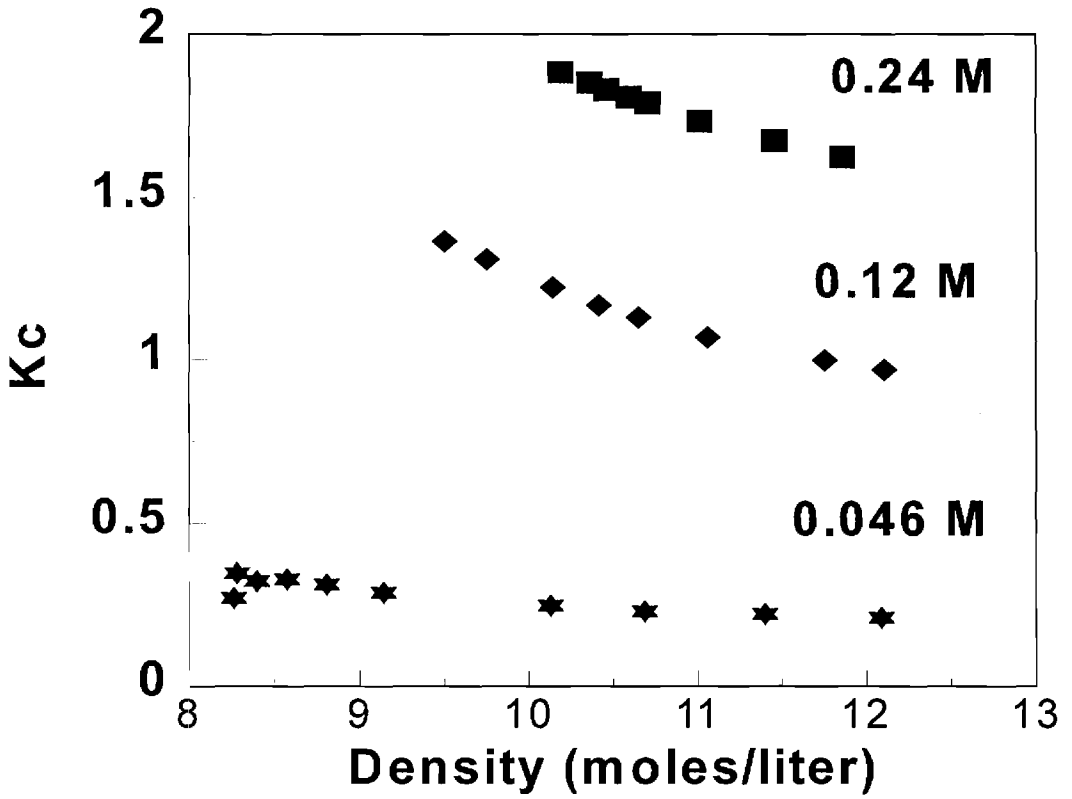

Figure 5. Equilibrium constant (K_c) as a function of density for 0.046 M, 0.12 M, and 0.24 M TFE in SCF ethane. (Equilibrium constant (K_c) as a function of density for Schiff base in TFE modified SCF ethane.)

It is important note that miscibility limits and critical mixture densities are different for each cosolvent system and for each cosolvent concentration; therefore, experimental data do not all begin at the same density. The same trend of shift in equilibrium constant was also found with ethanol and HFIP as cosolvents.

These results indicate large changes in tautomerization equilibrium may be obtained with small amounts of carefully selected cosolvents; however, the most interesting and informative result is the variation of the equilibrium constant with density. This effect can be seen in Figure 6 for ethanol and TFE modified SCF ethane solvent systems. The ethanol cosolvent system exhibits the largest density dependence. In all cases, the lowest concentration of added cosolvent results in a larger density effect on the equilibrium constant than the corresponding higher cosolvent concentrations. At the lowest cosolvent concentrations, miscibility limits permit the experiment to extend into the near-critical region of pure SCF ethane where local composition enhancements due to solute-solvent or solute-solute clustering are significant. At the higher concentrations, the experiments are further removed from this near-critical, compressible region. In addition, the shift in equilibrium constant towards the keto tautomer in the lower density regions

may be enhanced by the reduction in self-association of the alcohols which occurs in this same region. These free alcohols have a greater tendency to form intermolecular hydrogen bonds with the keto tautomer.

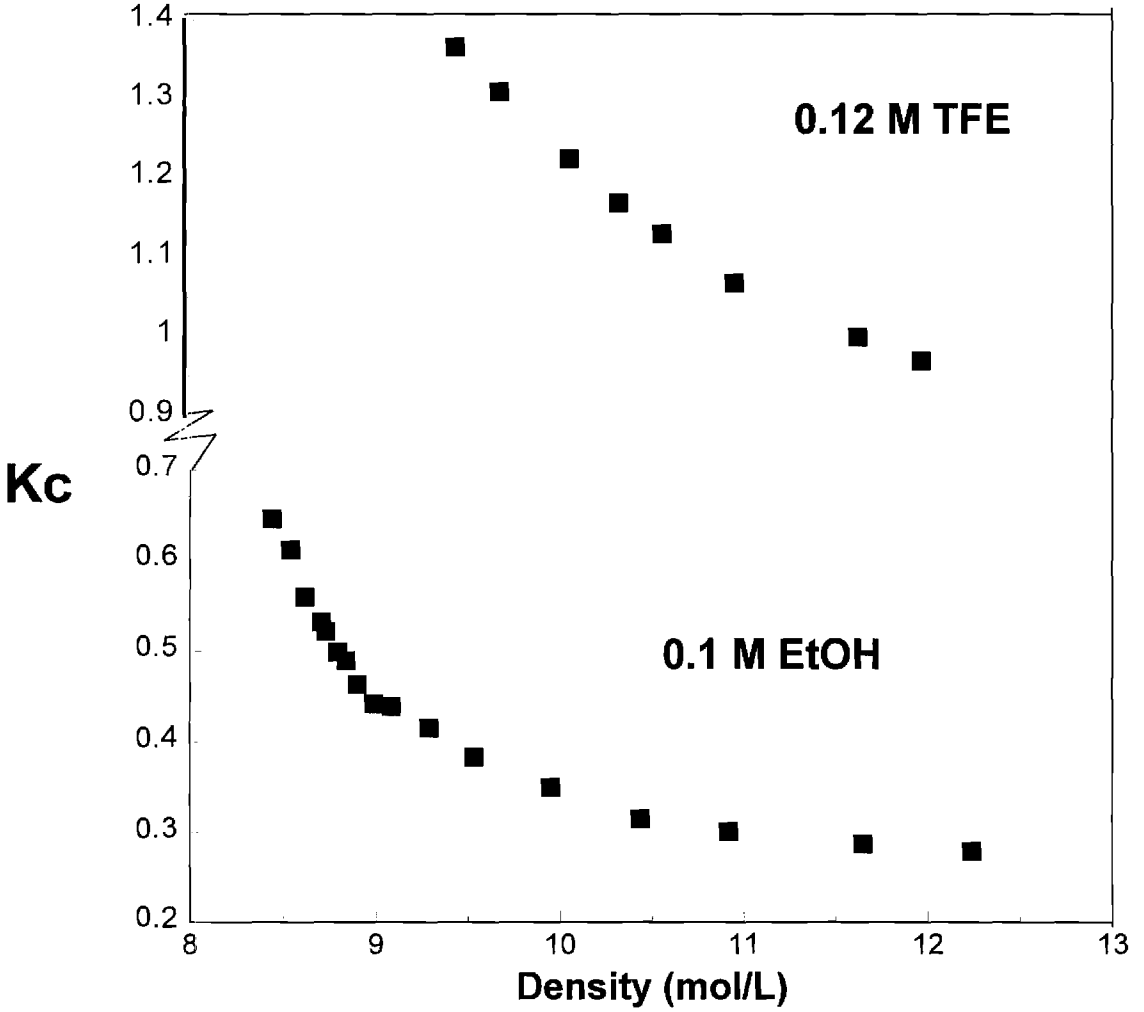

Figure 6. Equilibrium constant (K_c) as a function of density in cosolvent/SCF ethane in 0.1 M ethanol and 0.12M (Equilibrium constant (K_c) as a function of density in several cosolvent/SCF ethane systems.)

Therefore, the density effect observed can be attributed to a combination of factors. First, even in a compressed gas far from its critical point, density changes cause shifts in chemical equilibria due to changes in fugacity. However, in the near critical fluids we also have large effects due to local density and composition enhancements. Finally, hydrogen bonding of the keto tautomer to the cosolvent prevents tautomerization back to the enol form. As pressure is increased beyond the critical region, the equilibrium constant of hydrogen bonding decreases (Gupta et al., 1993; Kazarian et al., 1993a; Kazarian et al., 1993b), which would reduce the concentration of the hydrogen bonded keto form and result in a decrease in the equilibrium constant.

Modeling Based on General Chemical Physical Analysis

A physical-chemical model has been developed to characterize the behavior of the equilibrium constant as a function of density. Possible equilibria describing this solute in a cosolvent modified solvent system are shown below. The equilibrium constant K_1 is the actual tautomerization between the keto and enol forms of the Schiff base. The equilibrium constants K_2 and K_3 indicate the equilibrium between the cosolvent, a hydrogen bond donor, and the Schiff base tautomers which are hydrogen bond acceptors, along with the hydrogen bonded complex of each form. Finally K_4 is the equilibrium constant for the dimerization of the alcohol cosolvents. Other equilibria such as the formation of the higher self-associates of the alcohol cosolvents are neglected. In addition, HFIP exists in an equilibrium between two rotamer forms which have slightly different acidities. This equilibrium is know to vary with density (Kazarian and Poliakoff, 1995), however, should have negligible effects on the Schiff tautomerization and will be ignored.

$$\begin{aligned} K &\overset{K_1}{\leftrightarrow} E \\ K + H &\overset{K_2}{\leftrightarrow} KH \\ E + H &\overset{K_3}{\leftrightarrow} EH \\ H + H &\overset{K_4}{\leftrightarrow} HH \end{aligned} \tag{3}$$

Where K , E, and H designate the keto tautomer, enol tautomer, and cosolvent, respectively.

For simplification, only cosolvent systems with minimal self-association were modeled. The self association of fluorinated alcohols such as TFE is minimal, and with HFIP, there is essentially no dimerization at the concentrations used (Schrems et al., 1992; Kazarian et al., 1993b; Marco et al., 1994). Additionally, it was found from gas phase hydrogen bonding data between the fluoro-alcohols and various ketonic and enolic (phenolic, in particular, such as the enol form of the Schiff base used in this investigation) compounds that the third equilibrium (K_3) may be ignored (Abraham, 1993; Marco et al., 1994) because the equilibrium constant for hydrogen bonds between fluoro-alcohols and ketones is so much greater in comparison to that between the fluoro-alcohols and the phenolic compounds. This results in a model based on only two equilibrium constants:

$$K_1 = \frac{z_K \phi_K}{z_E \phi_E} \tag{4}$$

$$K_2 = \frac{z_{KH}\phi_{KH}}{z_K\phi_K z_H\phi_H} \tag{5}$$

where z_K, z_E, and z_{KH} are the true concentrations of the keto and enol tautomers of the Schiff base, respectively, and the keto hydrogen bonded complex; and the ϕ_K, ϕ_E, and ϕ_{KH} are the fugacity coefficients for these species.

In order to compare the model directly to the experimental results, an expression in terms of the experimental equilibrium constant was derived. For this derivation, it was assumed that the fugacity coefficients for each of the free Schiff tautomers (ϕ_K and ϕ_E) were equal and the free cosolvent concentration was constant, because in all cases the added cosolvent was in great excess of the Schiff base concentration. Then, the experimental equilibrium constant is given by,

$$K_{C,\exp} = \frac{\left[c_K + c_{KH}\right]}{\left[c_E\right]} \tag{6}$$

where the concentration of the keto tautomer is now a combination of the free and hydrogen bonded form of the tautomer. Then, the equilibrium constant calculated from a physical-chemical analysis becomes,

$$K_{C,calc} = K_1(1 + K_2 C_{\cos}\phi^*) \tag{7}$$

where

$$\phi^* = \frac{\phi_K\phi_H}{\phi_{KH}}, \tag{8}$$

K_1, K_2 are defined previously in equations 4 and 5, and C_{cos} is the bulk cosolvent concentration.

The fugacity coefficients were calculated from the Peng-Robinson equation of state (Reid et al., 1987). The binary interaction parameters (k_{12}) for the cosolvent/ethane systems were regressed from measured mixture densities and are given in Table 2. The binary interaction parameters for the cosolvent/Schiff complex in SCF ethane (k_{14}) arbitrarily were set equal to those for the cosolvent The binary interaction coefficient for the Schiff base/ SCF ethane (k_{13}) were set equal to 0.1 and all other interaction parameters were set equal to zero. The critical properties of ethane, ethanol (Reid et al., 1987), and TFE (Suresh et al., 1994) were obtained from the literature. The critical temperatures of HFIP, Schiff base, and Schiff base/cosolvent hydrogen bonded complex were estimated from Fedors method; the critical pressure and volume for the same compounds were estimated using the Joback method; and the acentric factor was estimated from the critical volume (Reid et al., 1987).

Table 2. Binary interaction parameters for SCF ethane/cosolvent systems regressed from experimental data using the Peng-Robinson equation of state.

Cosolvent in SCF Ethane	Cosolvent Composition (mol%)	k_{ij}
TFE	0.98	0.055
TFE	1.98	0.194
HFIP	0.68	-0.053
HFIP	1.36	0.033
EtOH	1.7	0.061

The equilibrium constant for the Schiff base keto tautomer/cosolvent hydrogen bonded complex (K_2) was assumed to be equal to the gas phase equilibrium constant for the same hydrogen bond donors with similar ketone compounds . These were obtained from the literature (Marco et al., 1994) and are given in Table 3. The gas phase data were given for 25 °C and were corrected to experimental conditions of 35 °C using gas phase enthalpy of formation literature data for the appropriate cosolvent/ ketone complex (Kivinen and Murto, 1969; Tucker and Christian, 1976). The equilibrium constant of tautomerization for the free Schiff base in the keto and enol forms was fit to the experimental data at the highest pressure data to avoid the effect of the anomalous behavior associated with the SCF critical region is absent.

Table 3. Equilibrium constants (K_2) for keto Schiff base/cosolvent hydrogen bonded complex at 25°C and corrected to 35°C.

Schiff Base/Cosolvent Hydrogen Bonded Complex	K_2 (L/mol) 22°C	K_2 (L/mol) 35°C
TFE	53	37
HFIP	250	154

The results of the model for the highest and lowest cosolvent concentration of TFE and HFIP are shown in Figures 7 and 8. With both cosolvent systems, the model agrees with the experimental data much better at the highest cosolvent concentration. In all cases, however, the model diverges from the experimental data in the area closest to the critical region. The model takes into account the changes in the K_C which result from changes in solution fugacity. Therefore, it is likely that the differences between the theory and the experimental data are a result of solute-cosolvent clustering resulting from local

composition enhancements and increases in hydrogen bonding approaching the critical region.

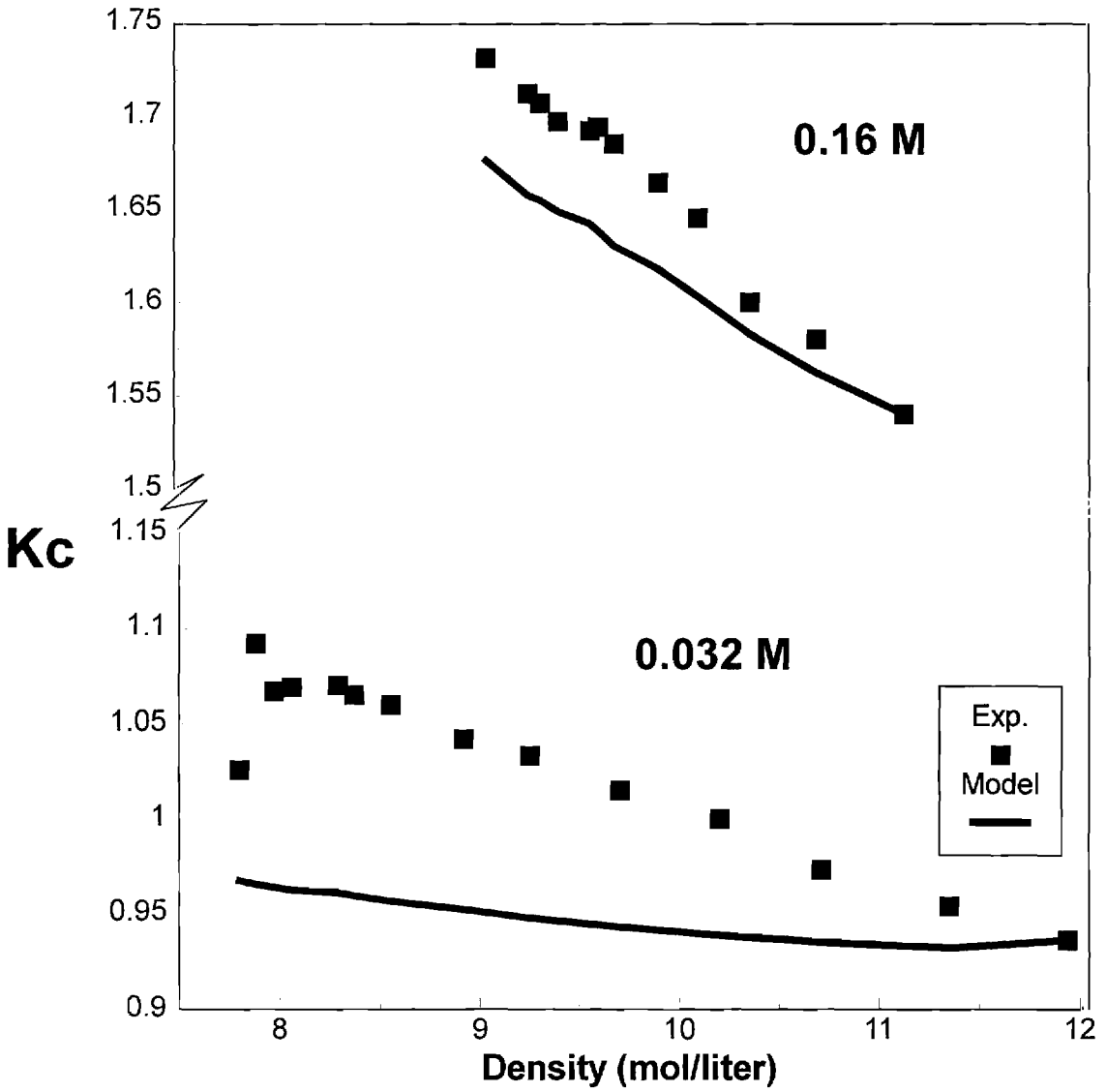

Figure 7. Results of equilibrium model:) 0.046 M and 0.24 M TFE/SCF ethane at 35°C. (Results of equilibrium model for Schiff base in TFE/SCF ethane solvent system.)

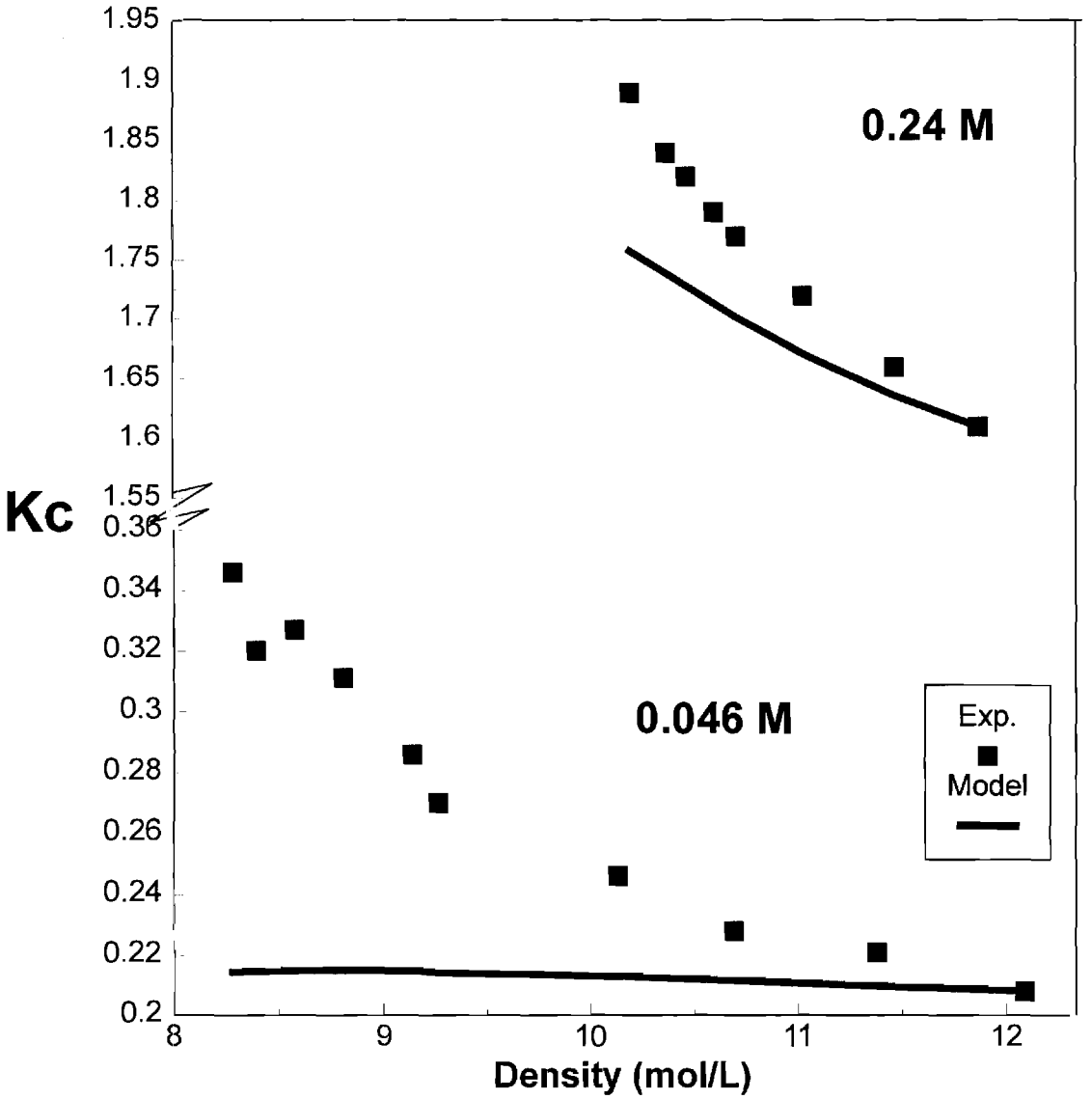

Figure 8. Results of equilibrium model: 0.032 M and 0.16 M HFIP/SCF ethane at 35°C. (Results of equilibrium model for Schiff base in HFIP/SCF ethane solvent system.)

A sensitivity analysis of the variables associated with the prediction of the equilibrium constant was performed to ensure that the differences between predicted and experimentally measured data were not due to inaccuracies in estimated values and literature constants. From the perturbation of estimated and literature values, it was found that the only variable in the model which could account for the magnitude of the discrepancy between the model and experiment was the cosolvent concentration. The local concentration of cosolvent needed for the model and experimental data to agree at the lowest density point for each data set is given in Table 4. The local composition enhancement needed for this local concentration is also given in this table. For both cosolvent/SCF systems modeled, the local concentration of cosolvent around the Schiff

base is equal (within experimental error) for the highest and lowest bulk cosolvent concentrations. This is consistent with the possibility of saturation of the local cosolvent concentration about the Schiff solute.

Table 4. Local composition enhancement and local concentration of cosolvent about the Schiff base from modeled results using chemical-physical theory.

Cosolvent	Bulk Concentration (M)	Mole Fraction Ratio x_{local}/x_{bulk}	Local Concentration (M)
TFE	0.046	9.2	0.423
TFE	0.24	1.7	0.401
HFIP	0.032	6.5	0.208
HFIP	0.164	1.3	0.213

There are several possible explanations for the observations above. At the highest cosolvent concentrations, miscibility limits dictate that the experiments are carried out beginning at densities which are well removed from the near critical region of the solvent system. In the cases of the lowest cosolvent concentrations, it was possible to extend the spectroscopic measurements into the critical region of the solvent system without phase splitting, where local composition enhancements are known to occur. In addition, with nearly 2 mol% of added cosolvent, the fluid is much less compressible in general than at lower cosolvent concentrations. It is also known that the equation of state fugacity coefficient calculations are more accurate at pressures well removed from the critical region.

PLANS FOR NEXT QUARTER

We shall study the reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in supercritical carbon dioxide and supercritical carbon dioxide modified with acetone. The nitrogen bearing compound PTAD has demonstrated superior reactivity and sensitivity to cosolvent additions. A convenient half-life of the reaction is expected under our conditions.

SUMMARY

Densities of binary supercritical mixtures of ethane with cosolvents, ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, have been measured by a constant volume apparatus. Measurements were made in the range 0.7 to 2.0 mol % cosolvent and pressure from 49.8 to 105.7 bar at 308.2 K. The tautomeric equilibrium constant was measured as a function of density in supercritical ethane modified with three different concentrations of hexafluoroisopropanol (HFIP). The measured equilibrium constant was found to be a function of fluid density and cosolvent concentration.

The position of Schiff base tautomeric equilibria was tuned from essentially one tautomer to another by modifying the solvent of pure SCF ethane with less than 2 mol% of cosolvents capable of hydrogen bonding interactions. For the cosolvents of EtOH, TFE, and HFIP, it was found that the equilibrium constant was a function of cosolvent concentration and mixture density. Modeling the equilibrium constants using general chemical-physical analysis results in differences in predicted and experimentally calculated equilibrium constants which are greater than accountable by theory alone. This evidence of solute-cosolvent clustering is consistent with the effects of density on hydrogen bonding (Kazarian et al., 1993). Hydrogen bonding has been shown to decrease with increasing density. A local composition enhancement of cosolvent about the Schiff base in the low density, near-critical region would result in an increased amount of hydrogen bonding which in turn shifts the equilibria to the keto tautomer. As the density of the solution is increased, the solute-cosolvent clustering decreases as the fluid becomes less compressible which also reduces the degree of hydrogen bonding. This decrease in hydrogen bonding in turn affects the keto-enol equilibria by decreasing the amount of the keto formation. Thus, it is possible to utilize density dependence of hydrogen bonding in SCF solutions to "tune" tautomeric equilibrium between the keto-enol forms of the Schiff base.

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SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator:	Professor Charles A. Eckert Georgia Institute of Technology School of Chemical Engineering & Specialty Separations Center (404) 894-7070
Initiation Date:	September 1, 1994
Period Covered by Report:	July 1, 1996 - September 30, 1996

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels - Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

OBJECTIVES

The goal of this work is to develop benign solvent/cosolvent systems for reactions which will achieve optimum denitrogenation in the pretreatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density, which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general (Johnston, 1989; Ely, 1991; Brennecke, 1989), as well as in

INTRODUCTION

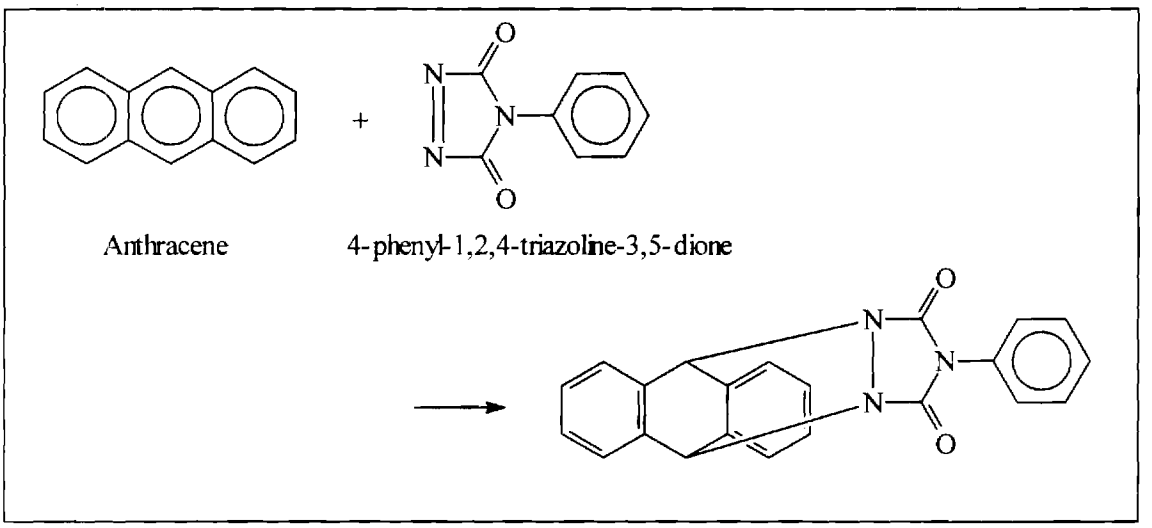
Over the last two decades, supercritical fluids have received an increasing amount of attention as a medium for carrying out chemical reactions (Savage, et al., 1995). The interest stems from unique advantages that supercritical fluids provide in the area of reaction rate control. A supercritical fluid, defined as a material at conditions above its critical temperature and pressure, is highly compressible at conditions near its critical point. The compressibility of the solvent can lead to large changes in reaction rate over small changes in pressure, and since pressure can be manipulated easily and precisely, pressure tuning represents a convenient route to rate control. Additional control of reaction rate can often be achieved through modification of the supercritical solvent with small amounts of a second solvent, designated as a "cosolvent".

Among supercritical solvents, CO_2 has received special attention due to the fact that in addition to a density which can easily be tuned over an order of magnitude it also provides a compelling combination of low cost, an easily accessible, thermally mild critical point and low toxicity. This combination of attributes is especially attractive to the food and pharmaceutical industries.

The reactants used to produce the rate data in this work follow a Diels-Alder reaction pathway, but the dienophile, named 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), is atypical. The reactive part of PTAD's structure is identical to maleimide, but has a pair of nitrogens at the bonding site instead of carbons. The reaction is illustrated in Figure 1. The nitrogen substitution results in reaction rates an order of magnitude higher than maleimide (Konovalov, et al., 1979), and has allowed the data presented in this work to be collected relatively swiftly. PTAD possesses another attractive aspect in addition to its high reactivity, and that is the fact that as a member of the Diels-Alder class of reactions it is an elementary bi-molecular reaction with a well established mechanism

(Sauer, 1967). This allowed the rate constant to be measured using simple pseudo first order data reduction techniques.

Figure 1. The Diels-Alder reaction of anthracene (diene) with 4-phenyl-1,2,4-triazoline-3,5-dione (dienophile.)



BACKGROUND

A great deal of theoretical work has been done toward rate predictive models capable of correlating rate constant data versus various solvent properties and thermodynamic variables. A review of this broad field of research is beyond the scope of this work, but a thorough discussion is provided in reviews by Savage and Clifford (Clifford and Bartle, 1996; Savage, et al., 1995). For the present purpose, an overview of the most important concepts will suffice as an introduction to ways in which the data in this work could be employed in future modeling efforts.

Arrhenius Activation Energy

The most traditional method of analyzing rate data is in terms of the Arrhenius equation, which is presented as equation (1). The Arrhenius equation represents the exponential relationship between rate constant and temperature, and can be used to extract information on the activation energy, which is defined as the energy needed to bring one mole of reactants from the ground state to the transition state of the reaction (Laidler, 1987a).

$$k_c = k_o e^{\left(-\frac{E_a}{RT}\right)} \qquad (1)$$

Solvent effects may be quantified using this relationship by determining the changes in activation energy that occur with changes in solvent properties (Hughes and Ingold, 1935, Tester, 1996). A solvent's effect on reaction rate is then discussed in terms of its ability to stabilize the transition state (Laidler, 1987b). Stabilization of the transition state through changes in solvent environment produces a lower energy of activation and a faster reaction. Prediction of solvent effects on reaction rates is accomplished through linear correlation of the log of the rate constant, which is proportional to the activation energy, versus an appropriate solvent property. Examples of solvent properties against

which correlations can be made include density, dielectric constant, or a solvatochromic parameter such as α, which measures a solvent's hydrogen bond donating ability; β, which measures hydrogen bond accepting ability; or π^*, which measures polarity/polarizability (Kim and Johnston, 1987a). A drawback of this method is that a large amount of experimental rate data needs to be collected in order to apply the technique. The data must cover a wide range of solvent types and reaction conditions before solvent effects can be predicted for an uncorrelated solvent. Even if the necessary data is available, the reaction rate predicted for the new solvent may possess significant error due to unusual specific interactions between solvent and reactants.

Transition State Theory

A more rigorous approach to the prediction of solvent effects on reaction rate is provided by transition state theory. In this treatment, it is assumed that the rate of reaction is dependent on an equilibrium established between the two reactant molecules and an "activated complex".

$$A + B \leftrightarrow M \leftrightarrow \text{Products}$$

The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities. (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

$$K_{eq} = \frac{[M]}{[A][B]} \frac{\gamma_M}{\gamma_A \gamma_B} \qquad (2)$$

Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

$$k = k_O \frac{\gamma A \gamma B}{\gamma M} \qquad (3)$$

In equation (3), the rate constant k is a product of k_o, the rate constant in a standard state environment (where all activities are unity), and the activity coefficients of the reactants and activated complex at the actual conditions of the reaction. This relationship cannot predict absolute reaction rates, but does have the potential to predict changes in the rate constant with a change in reaction conditions. The ability of this relationship to predict reaction rates relative to the rate at a standard state is limited only by the validity of the solution theory used to define the activity coefficients. If a solution theory possessing a small number of adjustable parameters is applicable to a given reaction, transition state theory has the potential to provide solvent effect predictions with less data than correlations based on Arrhenius activation energies.

Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, and so it can be used to provide a simple example of how (3) can be modified for practical application (Hildebrand and Scott, 1962); Hildebrand, 1964 #105]. In the Scatchard and Hildebrand model, a solubility parameter, δ, is defined for the solvent and each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When δ is related to the activity of a component, the following simple relationship results.

$$RT \ln \gamma_j = v_j \left(\delta_j - \bar{\delta} \right)^2 \qquad (4)$$

$$\bar{\delta} \equiv \sum_i^m \Phi_i \delta_i \qquad (5)$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\bar{\delta}$ is to an excellent approximation the solubility parameter of the solvent δ_S.

$$\ln\left(\frac{k}{k_O}\right) = \frac{v_A\left(\delta_A - \delta_S\right)^2 + v_B\left(\delta_B - \delta_S\right)^2 - v_M\left(\delta_M - \delta_S\right)^2}{RT} \qquad (6)$$

Local Density Enhancement

The rate predictive model based on regular solution theory would probably not work in the near critical region of a solvent, due to the tendency of a near critical solvent to exhibit densities in the vicinity of the reactants that are higher than the density of the bulk fluid. This local density enhancement represents a significant change in solvent properties unrelated to dispersion forces, and so the regular solution theory based model would fail to account for its effects.

Local density enhancement is brought about by short range solute-solvent interactions at solvent densities between 0.4 and 0.8 times the critical density (Brennecke, et al., 1990; Eckert and Knutson, 1993; Kim and Johnston, 1987b; Paulaitis and Alexander, 1987). Local density enhancement has the effect of creating local or "true" reactant concentrations which differ from the concentrations found in the bulk fluid.

Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and subsequently correcting measured rate constants for these enhancement effects (Kim and Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO_2, for example, suggests that in at least some cases changes in the rate constant near the critical pressure may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories. One can choose to model reaction rates using the Arrhenius approach, transition state theory, or other methods not discussed here. But whatever approach is used, good rate constant data is needed to provide a test for the models that are developed. This work has provided such data, with the intention of applying it to modeling efforts in the near future.

INSTRUMENTATION AND EQUIPMENT

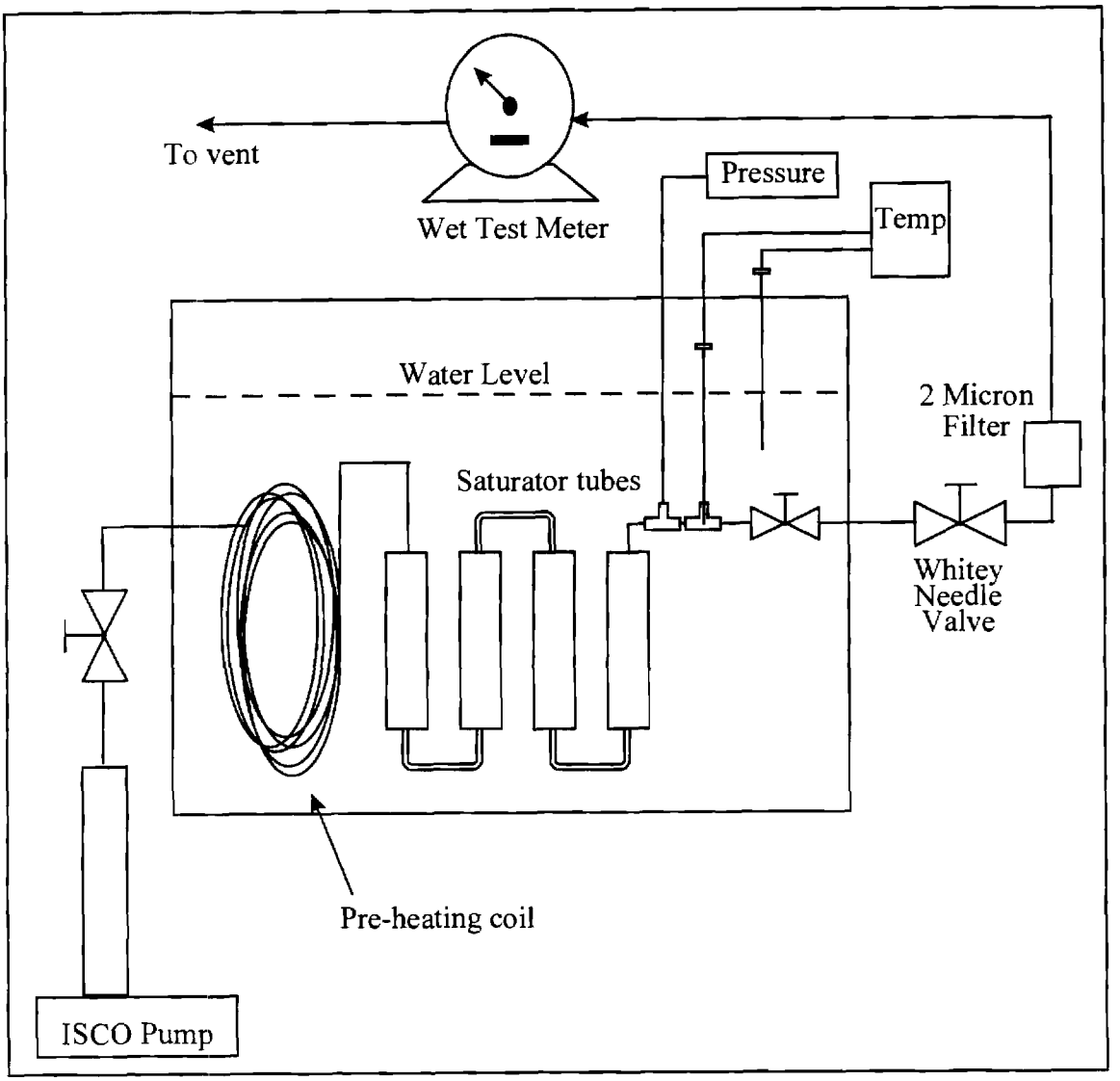
Materials

The reactants and liquid solvents used for this investigation were supplied by Aldrich Chemical Company, and were used as received. The reactants were 4-phenyl-1,2,4-triazoline-3,5-dione (98% pure) and anthracene (97% pure). The liquid solvents were acetone (99.9% HPLC grade), acetonitrile (99.9+% HPLC grade) and chloroform (99.9+% HPLC grade). The carbon dioxide used was SFC grade, supplied by Matheson Gas Products. It was passed through a Matheson Gas Products Model 450B Gas Purifier before use.

Solubility Apparatus

In order to insure that all PTAD placed in the cell was actually dissolved into the fluid phase during an experiment, it was necessary to determine experimentally the saturation solubility of PTAD in CO_2 at 40 °C and various pressures. The apparatus constructed for this purpose followed a design described in a previously published paper and is illustrated in Figure 2 (Johnston, et al., 1982).

Figure 2. Apparatus for determining the solubility of PTAD in supercritical CO_2.



Tubing and fittings were of stainless steel and were manufactured by Swagelok. Solid PTAD samples were collected from solution by precipitation across a Whitey SS-31RS4 needle valve into a NuPro 2 micron inline filter. Delivery of CO_2 was accomplished using an ISCO Model 260D syringe pump. Volumetric flows of CO_2 were measured using an Alexander Wright - London wet test meter Model Midget M.6109. The wet test meter was calibrated by decompressing a known mass of CO_2 of known density through the meter. The meter was found to be accurate to +/- 0.3 cc at STP.

Pressure was measured using a Druck PDCR 911 transducer attached to a Druck DPI 60 digital readout. The pressure transducer and readout were calibrated using a Ruska dead weight type apparatus, and were found to be accurate to +/- 1 psi.

Temperatures of water bath and CO_2 stream were measured using Omega Type K grounded thermocouples attached to a model HH-25KC readout with resolution to 0.1 °C. The sheath of the thermocouple measuring the temperature of the CO_2 stream was in direct contact with the stream. Both the solution thermocouple and the water bath thermocouple were calibrated against a platinum resistance thermometer, and were found to be accurate to +/- 0.1 °C. The temperature of the water bath was maintained within +/- 0.1 °C using a Bayley Instrument Co. Model 123 precision temperature controller.

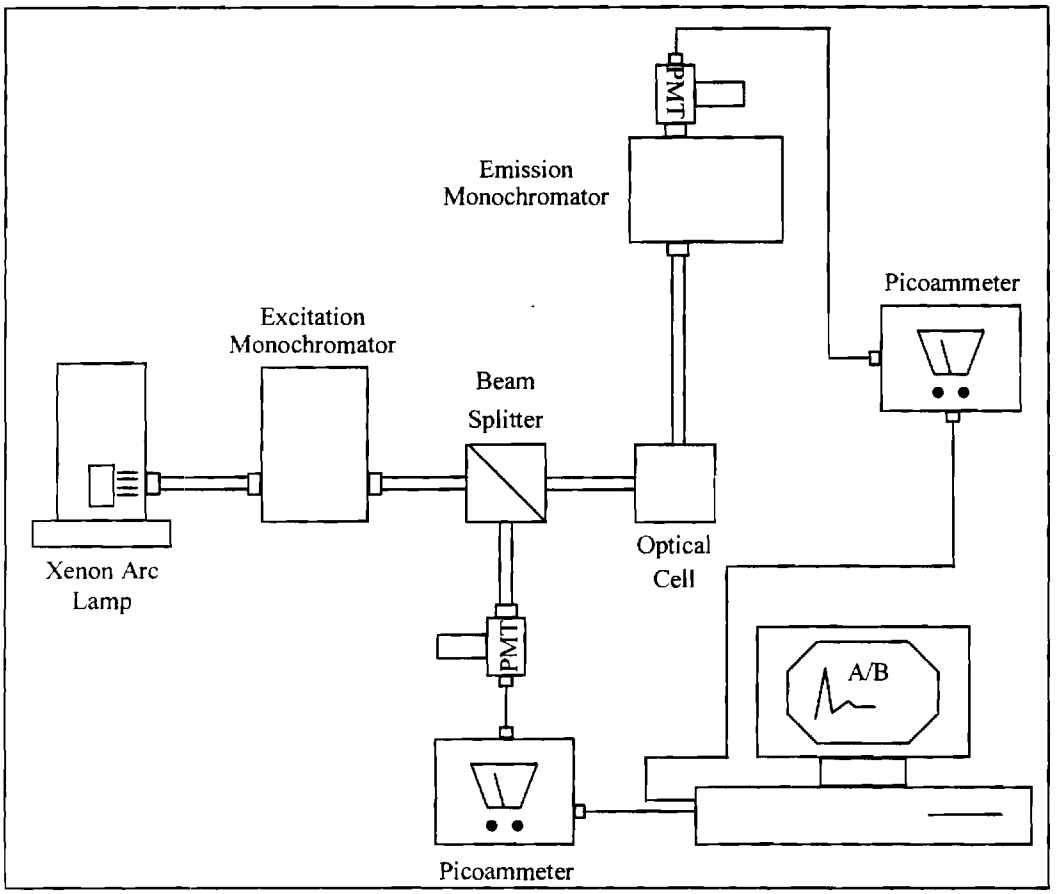
Fluorescence apparatus

Reaction kinetics were followed spectroscopically by fluorescence. The equipment used to make these measurements was configured in the manner illustrated in Figure 3. Light from a Spectral Energy SX1000-2 Xenon UV lamp was passed through a Kratos Analytical Model GM252 monochromator, producing an excitation light beam at a single wavelength. The excitation beam was split into two beams using a half-silvered mirror, producing an excitation beam and a reference beam.

The reference beam was directed into a Kratos D 500 Side-On Photomutiplier Tube (PMT), which produced an amperage output measured using a Keithley Instruments 414A Picoammeter. The excitation beam was directed into the optical cell containing the experimental sample of anthracene. The fluorescence of anthracene produced an emission beam of light, which was directed into a second GM252 monochromator where it was filtered to a single wavelength of light. The filtered emission wavelength was directed into a second D 500 PMT, which produced an amperage output that was measured using a Keithley 485 Autoranging Picoammeter.

Each Picoammeter produced an analog output voltage in proportion to beam intensity, designated as Signal A for the emission beam intensity and as Signal B for the reference beam intensity. The ratio of these two signals - A/B - varied with changes in

Figure 3. An overview of the high pressure fluorescence apparatus used for kinetic measurements.



fluorescent emission intensity, but did not vary with fluctuations in lamp intensity. The emission intensity of the sample was recorded as the numerical value of the ratio A/B.

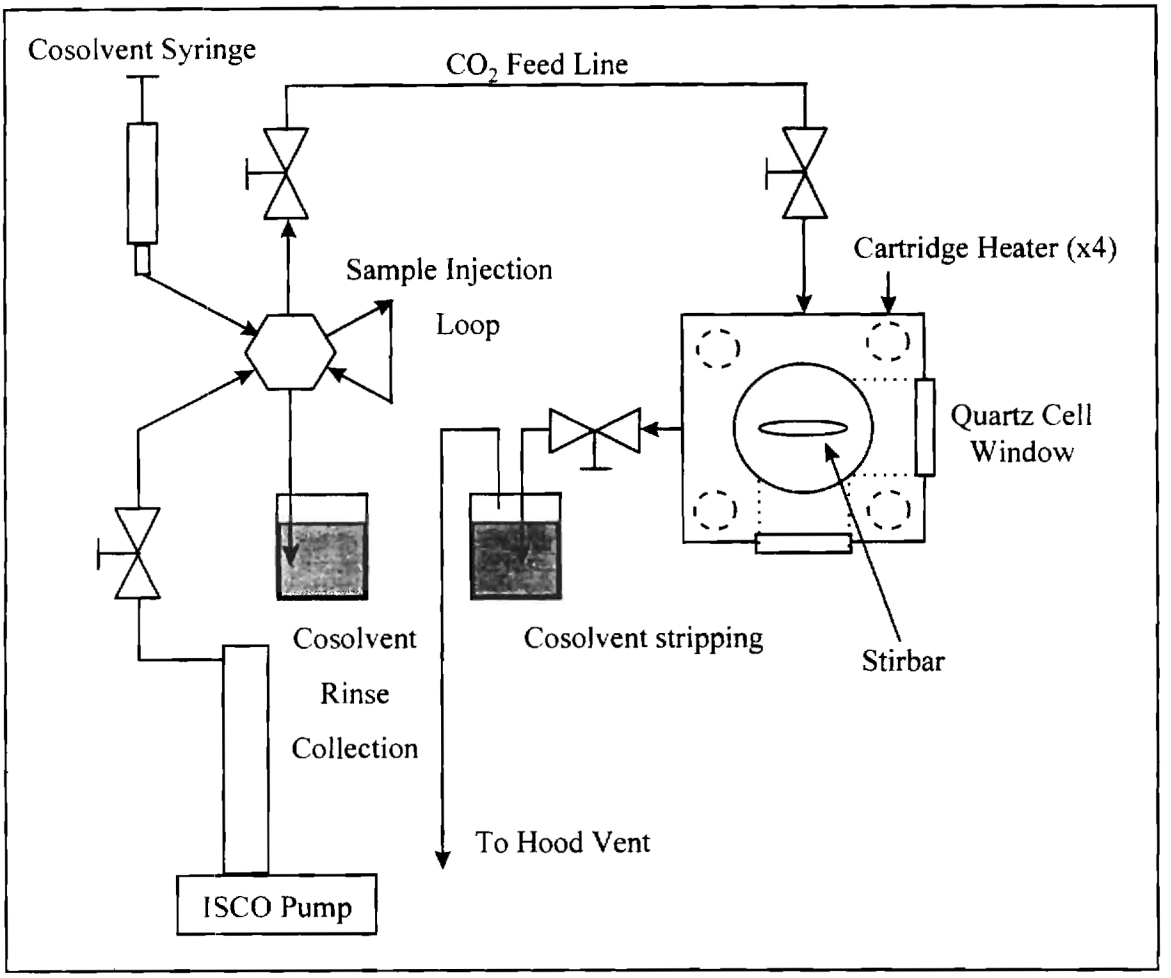
The optical cell was constructed from 316 stainless steel and was configured for solvent introduction and removal as in Figure 4. The windows were made from quartz, and were positioned at right angles to one another so that as little of the excitation light as possible would exit the cell with the emission light. The seals for cell windows were o-rings made of Teflon. All tubing and fittings were stainless steel and were manufactured by Swagelok or HiP. CO_2 was delivered to the cell using an ISCO Model 260D syringe pump which fed through a Valco 6-port sample injection valve. A Teflon coated stirbar was used to provide agitation of the cell contents.

Pressure was measured using a Druck PDCR 911 transducer attached to a Druck DPI 60 digital readout. The pressure transducer and readout were calibrated using a Ruska dead weight calibration apparatus, and were found to be accurate to +/- 1 psi.

Internal temperatures were measured using a 1/16" grounded Omega Type K thermocouple in an inconel sheath. It was mounted with its tip in direct contact with the experimental solution. The thermocouple was attached to a readout with resolution to 0.1 °C. The thermocouple was calibrated against a platinum resistance thermometer, and was found to be accurate to +/- 0.1 °C.

Internal temperature was controlled using a second 1/8" Type K thermocouple mounted with its tip in the steel of the cell block. The thermocouple was attached to an Omega CN9000A controller which used four cartridge heaters mounted in the steel of the cell block to maintain cell temperature. Temperature control of cell contents was within +/- 0.2 °C.

Figure 4. An overview of the optical cell, and the apparatus used for the injection of cosolvents.



PROCEDURES

Solubility Measurements

The apparatus was prepared for use by packing the four saturator tubes with PTAD, using plugs of fiberglass at the ends of each tube to prevent migration of the solid. The water bath was then filled, and the temperature of the water bath was allowed to equilibrate overnight. With the ISCO running in constant pressure mode, the saturator line was brought to a specific pressure and was allowed to equilibrate with the PTAD for 30 min. The needle valve was then opened to the point where CO_2 flowed at a liquid rate of approximately 0.1 ml/min. The apparatus was shut down when approximately 30 liters of CO_2 (STP) had flowed through the wet test meter. The STP volume of CO_2 that flowed through the wet test meter and the weight of PTAD that had collected in the needle valve and filter were recorded.

Kinetic Analysis

The reaction of PTAD with anthracene is an elementary bi-molecular reaction, so if one reactant is present in excess pseudo-first order kinetics can be used to extract rate constants from concentration versus time data. UV spectroscopy was used for the analysis of the reaction rate of PTAD and anthracene in liquid solvents (Konovalov, et al., 1979) by following the decay of PTAD over time. But in order to apply pseudo first-order kinetics, anthracene needed to be present in excess. Though an excess of anthracene is possible in liquids, in supercritical CO_2 PTAD solubility is on the order of 10^{-3} mol/L, and anthracene solubility is on the order of only 10^{-5} mol/L. The dilemma was solved by using fluorescence spectroscopy instead of UV. Fluorescence spectroscopy can detect concentrations of anthracene as low as 10^{-7} mol/L, making it possible to have PTAD present at an initial excess of 100:1 and still follow a change in anthracene concentration over two orders of magnitude.

In order to conveniently calculate the rate constant of the reaction from fluorescence emission data, it is possible to use Beer's law to relate pseudo first order rate constants

directly to changes in emission signal. Solution of the differential equation (9) relating concentration changes of one reactant to the concentration of both reactants leads to (10) when PTAD is assumed to be in great excess and therefore constant throughout the reaction.

$$\frac{dc_{AN}}{dt} = k_c c_{PTAD} c_{AN} \qquad (9)$$

$$\ln\left(\frac{c_{AN}}{c_{ANo}}\right) = -\left(k_c c_{PTADo}\right)t \qquad (10)$$

Simple experiments involving incremental additions of anthracene to a liquid solvent indicated that the fluorescence of anthracene follows Beer's Law (11) as long as the anthracene is dilute (i.e. less than 10^{-5} mol/l), and the emission wavelength monitored is well removed from wavelengths at which self-absorption may occur. The path length l in Beer's Law does not change during a run, and so (11) may be written once for initial conditions, and again for an arbitrary time t. The ratio of these equations may be substituted into (10), leading to (12). Equation (12) allows the pseudo first order rate constant to be derived directly from emission data without knowing the exact concentration of anthracene in the cell.

$$e = \varepsilon l c_{AN} \qquad (11)$$

$$\ln\left(\frac{e_{AN}}{e_{ANo}}\right) = -k_c c_{PTADo} t \qquad (12)$$

Cell Volume Determination

In order to obtain accurate values of c_{PTADo} for use in (12), it was necessary to know the volume of the cell and associated tubing. A stirbar was placed into the cell, and the cell

was filled with pure CO_2 to a known temperature and pressure. The Bennedict-Webb-Rubin equation of state (Ely, et al., 1989) was used to estimate the density of the fluid, and the CO_2 was then released from the cell through a calibrated wet test meter. The experiment was repeated three times. Calculations using the known STP CO_2 volume, cell and wet test temperatures, cell pressure and cell CO_2 density produced a cell volume of 16.5 cc, +/- 0.1 cc.

Kinetic Measurements in Liquids

An anthracene stock solution was prepared in acetone, and a PTAD stock solution was prepared in the solvent being used in the experiment. A quantity of the anthracene stock solution was placed into the optical cell using a Gilman uL Pipetman accurate to 0.8%. The cell was dried under vacuum for 5 minutes. Visual inspection was used to determine that the cell was dry.

Because the reaction proceeds so quickly, it was necessary to avoid introducing reactants into the optical cell before the solvent had reached steady state temperature. For this reason, the loading of the cell was performed in three steps. First, a quantity of anthracene stock was placed in the bottom of the cell, and was allowed to dry. Next, a known volume of solvent was introduced using a syringe accurate to +/- 0.05 ml. the cell was sealed and the solvent was brought to temperature. Finally, data acquisition software was started and a microliter quantity of PTAD stock was placed into the cell using the Gilman pipette. The cell was resealed and the reaction was observed for approximately 20 minutes. In between runs, the cell was cleaned thoroughly with acetone.

Kinetic Measurements in Pure Supercritical CO_2

Stock solutions of PTAD and anthracene were prepared in acetone. A fresh PTAD stock solution was prepared each day. A known quantity of each stock solution was placed into the optical cell using the Gilman Pipet, with PTAD in excess by a factor of 40. The cell was dried under vacuum for 5 minutes. Care was taken to insure that the two stock

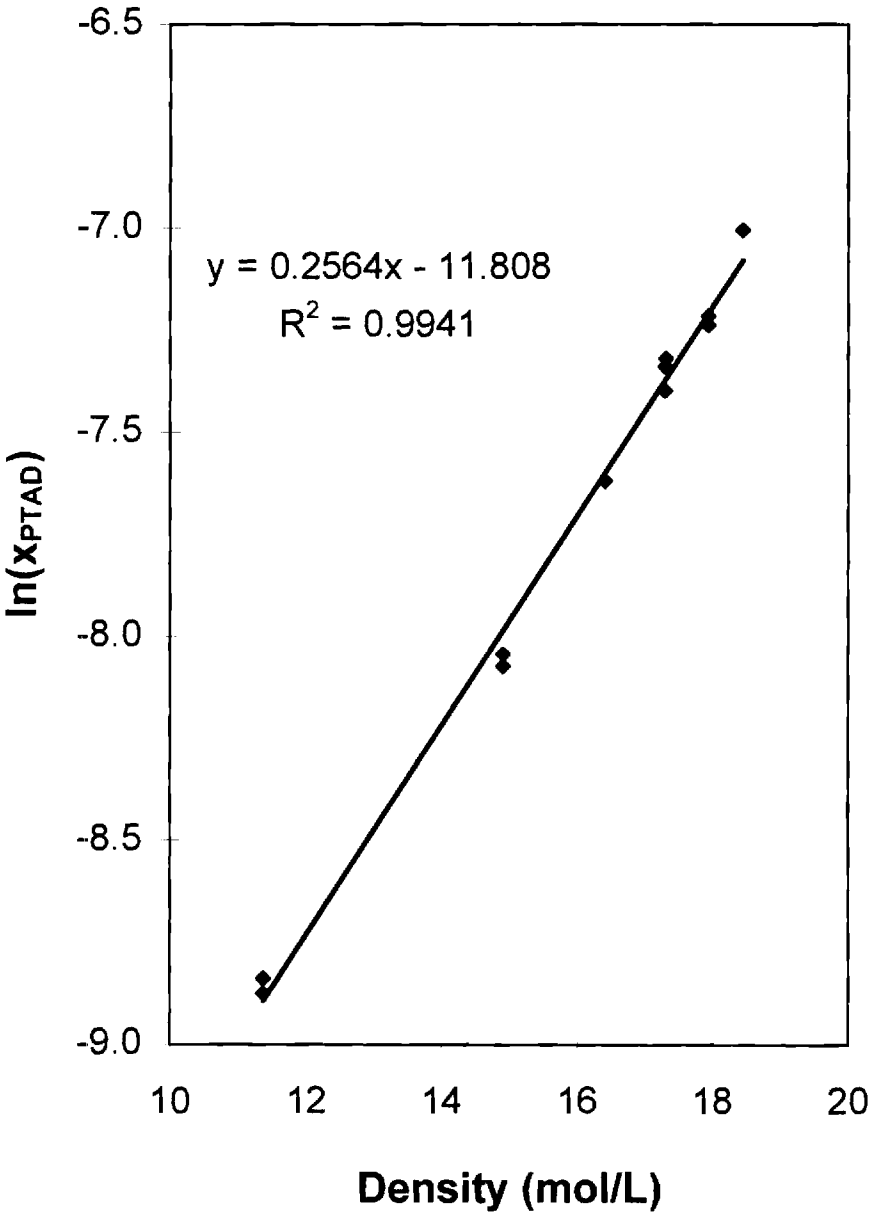
solutions did not contact one another during drying. Dryness of the cell was determined by visual inspection.

Data acquisition software was started, and the cell was pressurized with pure CO_2 from the ISCO syringe pump. The time and pressure at which the cell reached 40.0 °C was recorded, and the reaction was observed for about twenty minutes. Kinetic analysis was performed only on data collected while the cell was at 40.0 +/- 0.2 °C. The cell was cleaned thoroughly with acetone between each experiment.

Solubility of PTAD in Supercritical CO_2

Results obtained for the solubility of PTAD in CO_2 at 40 °C are plotted in Figure 5. The lowest pressure at which the solubility of PTAD was measured was 90.7 bar, but during the course of kinetic experimentation it became clear that the value of reaction rate constants at pressures as low as 75 bar (the critical pressure of CO_2) were of interest. The solubility of PTAD in CO_2 at lower pressures was estimated by the extrapolation of existing data using a linear regression through the log of solubility versus density. The Bennedict-Webb-Rubin equation of state was used to estimate the density of pure CO_2 for each existing experimental solubility point.

Figure 5. The solubility of PTAD in pure CO_2 at 40 °C.



Liquid Solvents

Chloroform is a polar, slightly protic solvent. Though acetonitrile is more polar that chloroform, it is not protic. These two liquid solvents were selected for use in the liquid portion of the work, and results suggest that the PTAD/anthracene reaction is highly sensitive to acidity, but not to the polarity of a solvent. A plot of $-\ln(e/e_o)$ vs. time for the acetonitrile data is presented as Figure 6, and demonstrates that the reaction followed reproducible pseudo first-order kinetics. The Arrhenius plot presented as Figure 7 was used to regress activation energies and pre-exponential factors for each solvent, and the rate constant for each solvent was determined for 25 °C. The results of these calculations are presented, along with literature values, in Table 1. The rate constants produced with fluorescence spectroscopy are in general agreement with those produced by UV. The reaction is faster in the more protic chloroform by a factor of 16.

Figure 6. The reaction of PTAD with anthracene in liquid acetonitrile. $[PTAD]_o$ = 1.06E-03 mol/l, [PTAD]/[AN] = 40:1.

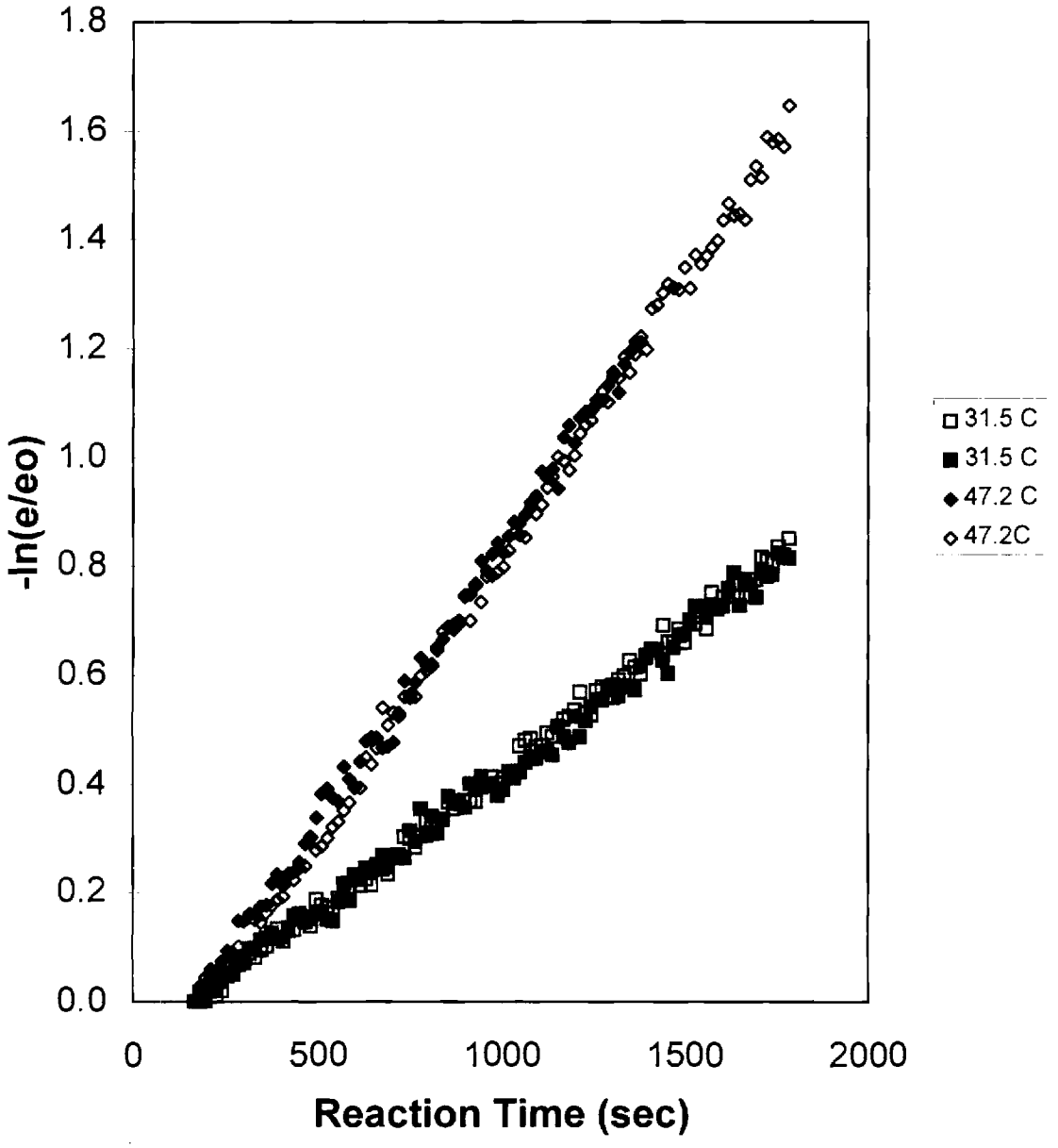


Figure 7. Activation energies for the reaction of PTAD with anthracene in two liquid solvents

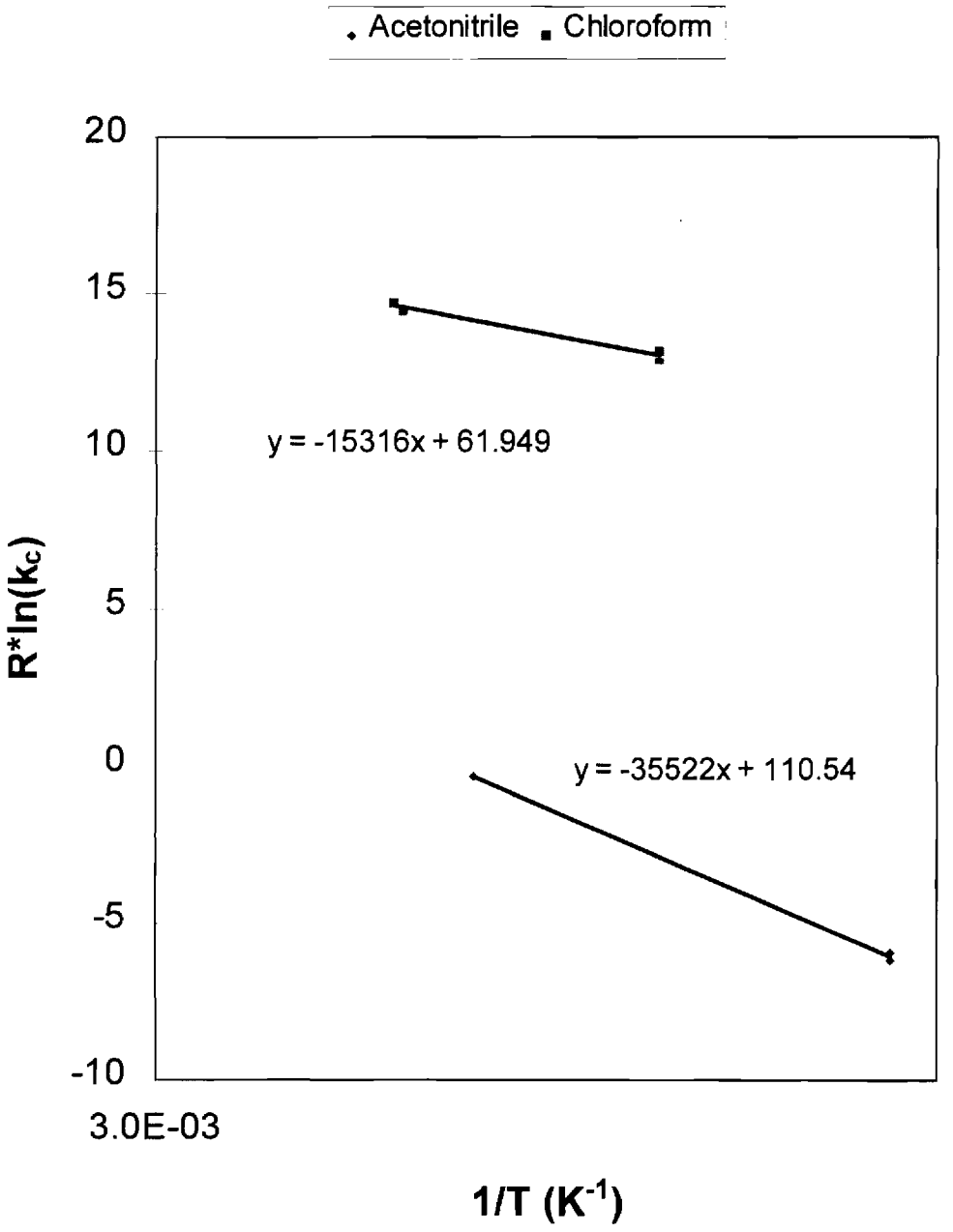


Table 1. Rate constants at 25 °C for the reaction of PTAD with anthracene in two liquid solvents. * (Konovalov, et al., 1979).

	Acetonitrile	Chloroform
ko (1/M s)	5.95E+05	1.90E+03
Ea (kJ/mol)	35.5	15.3
k25 °C	0.36	3.6
k25 °C*	0.32	5.1
% Difference	11	-29

Supercritical CO_2

Rate constants were obtained for the reaction in pure CO_2 at 40 °C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 216 bar. Rate constant values are plotted in Figures 8 and 9. Two views are provided for the purpose of making the cluster of points at 95 bar more readable. The reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are 25 times greater than those above 110 bar. The average estimated error in rate constant values was 15% at higher pressures, increasing to 20% near the critical pressure. Details of the method used to estimate experimental errors may be found in Appendix C.

Figure 8. The rate constants for the reaction of PTAD with anthracene in pure CO_2 at 40 °C.

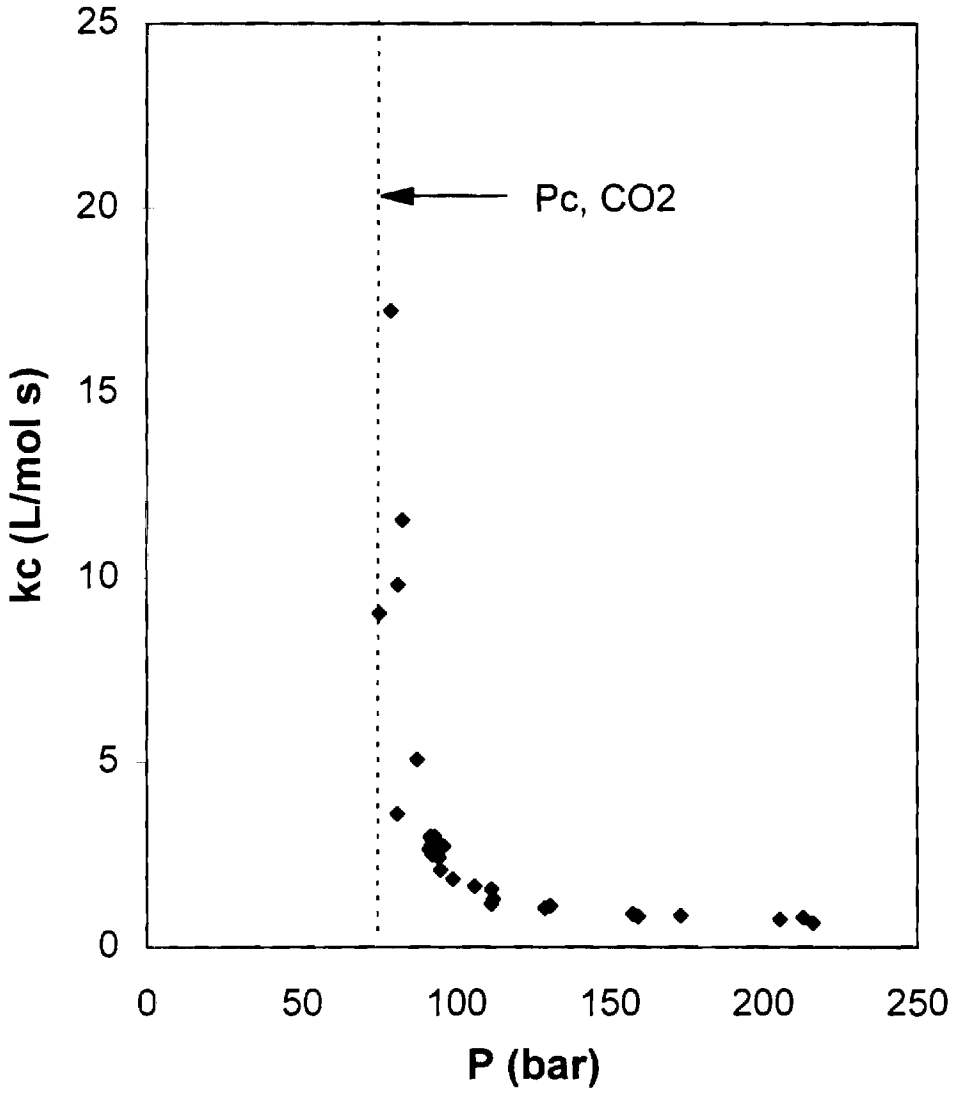
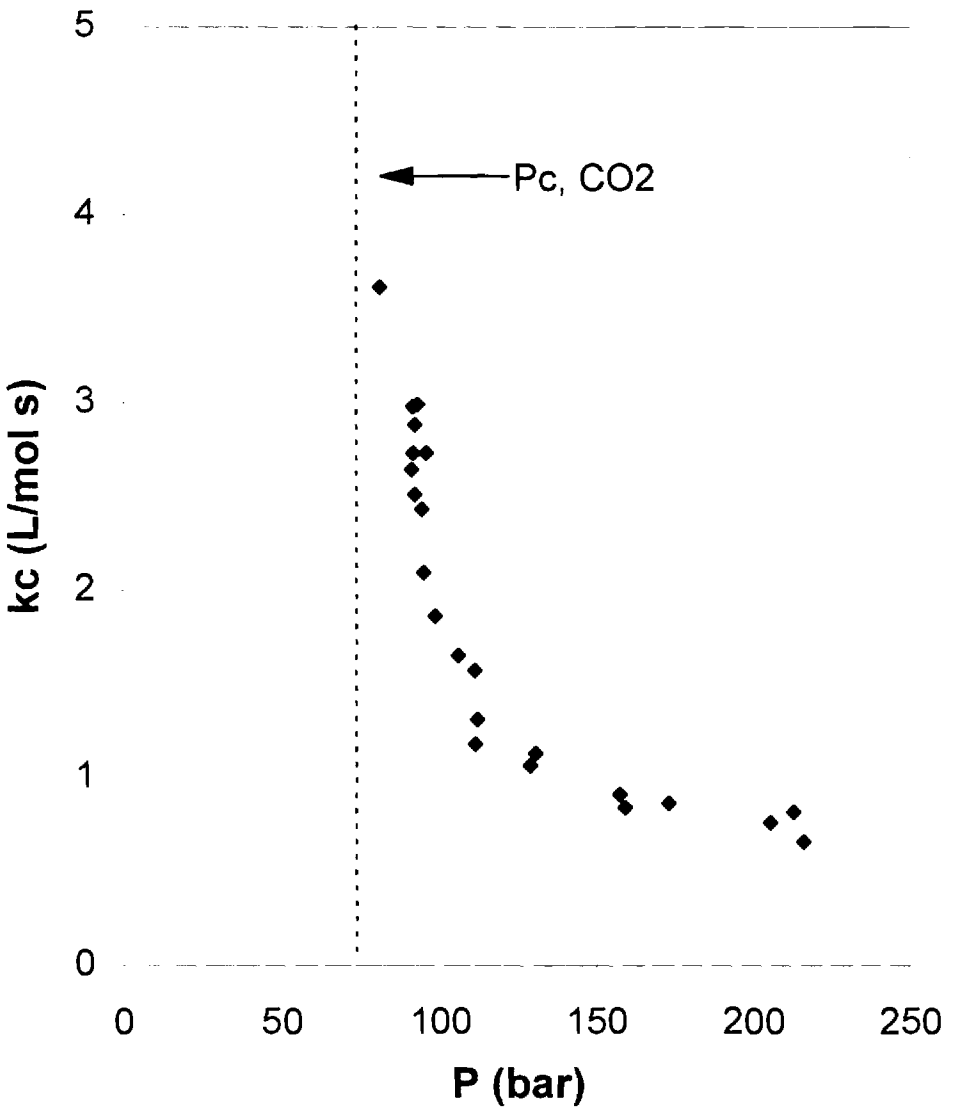


Figure 9. Rate constants having values less than 5 l/mol s for the reaction of PTAD with anthracene in pure CO_2 at 40 °C.



Conclusions

The rate constant for the reaction of PTAD with anthracene in supercritical CO_2 decreases as system pressure increases from the critical pressure of CO_2. The almost linear change of $\ln(k_c)$ versus density at high densities, and the modest increase in upward curvature at densities below the critical pressure suggest that solvation of the transition state by CO_2 is the most important phenomenon driving changes in the rate constant. The upward curve of the data in the low density region supports the concept of local density enhancement in the critical region.

APPENDIX A

Table A-1. Rate constants for the reaction of PTAD with anthracene in two liquid solvents.

Solvent	Temp (°C)	$[PTAD]_o$ $x10^3$ (mol/L)	$[AN]_o$ $x10^5$ (mol/L)	k_c (1/Ms)
Acetonitrile	31.5	1.06	6.93	0.49
Acetonitrile	31.5	1.06	6.93	0.48
Acetonitrile	47.2	1.06	6.93	0.95
Acetonitrile	47.2	1.06	6.93	0.96
Chloroform	40.0	1.51	3.76	4.7
Chloroform	40.0	1.51	3.76	4.9
Chloroform	50.4	1.51	3.76	5.9
Chloroform	50.0	1.51	3.76	5.7

Table A-2. Rate constants for the reaction at 40 °C of PTAD with anthracene in pure CO_2 solvent.

P (bar)	$[PTAD]_o$ $x10^3$ (mol/L)	$[AN]_o$ $x10^5$ (mol/L)	k_c (1/Ms)
75.1	0.14	1.29	9.0
78.9	0.14	1.29	17.2
81.0	0.36	3.42	3.6
81.1	0.14	1.29	9.8
82.6	0.13	1.29	11.6
87.4	0.52	3.23	5.1
91.3	1.21	3.03	2.6
91.5	1.21	3.03	3.0
91.7	1.21	3.03	2.7
92.2	1.21	6.06	2.5
92.3	1.21	3.03	2.9
93.1	1.34	6.45	3.0
94.4	1.21	3.03	2.4
94.9	1.25	6.06	2.1

Table A-3. Continued listing of rate constants for the reaction at 40 °C of PTAD with anthracene in pure CO_2 solvent.

P (bar)	$[PTAD]_o$ x10^3 (mol/L)	$[AN]_o$ x10^5 (mol/L)	k_c (1/Ms)
95.9	1.21	6.06	2.7
98.7	1.27	6.06	1.9
106.1	1.26	6.06	1.7
111.5	1.21	3.03	1.6
111.5	1.21	3.03	1.2
112.2	1.21	3.03	1.3
129.0	1.21	3.03	1.1
130.7	1.21	3.03	1.1
157.5	1.21	3.03	0.91
159.2	1.21	3.03	0.84
173.2	1.21	3.03	0.86
205.5	1.21	3.03	0.76
213.0	1.21	3.03	0.81
216.1	1.21	3.03	0.66

Table A-4. The solubility of PTAD in Pure CO_2 at 40 °C.

Temp (C)	Press (bar)	Pure CO_2 Density (mol/L)	x_{PTAD} $x10^4$ unitless
40.0	90.7	11.37	1.4
40.0	90.7	11.37	1.5
40.1	104.5	14.91	3.1
40.1	104.5	14.91	3.2
40.1	121.7	16.42	4.9
40.0	139.0	17.32	6.6
40.1	139.0	17.30	6.5
40.1	139.0	17.30	6.1
40.1	156.2	17.94	7.4
40.1	156.2	17.94	7.2
40.1	173.5	18.45	9.1

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 894-7070

Initiation Date: September 1, 1994

Period Covered by Report: October 1, 1996 - December 31, 1996

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels - Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

During this quarter, measurement of the density dependence of the kinetic rate constant for PTAD and anthracene in supercritical solvents was continued. Having completed studies of rates versus density in pure CO_2 at 40C, attention was focused on CO_2/cosolvent mixtures. Experiments were performed using binary mixtures of CO2 and either chloroform or acetone as cosolvent. Cosolvent concentrations were varied between 0.00826 mol/L and 0.0826 mol/L. The cosolvents produced no significant change in the rate constant over that of pure CO_2 at these concentrations.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCF's via kinetic measurements using well characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

BACKGROUND

A great deal of theoretical work has been done toward rate predictive models capable of correlating rate constant data versus various solvent properties and thermodynamic variables. A review of this broad field of research is beyond the scope of this work, but a thorough discussion is provided in reviews by Savage and Clifford (Clifford and Bartle, 1996; Savage, et al., 1995). For the present purpose, an overview of the most important concepts will suffice as an introduction to ways in which the data in this work could be employed in future modeling efforts.

Arrhenius Activation Energy

The most traditional method of analyzing rate data is in terms of the Arrhenius equation, which is presented as equation (1). The Arrhenius equation represents the exponential relationship between rate constant and temperature, and can be used to extract information on the activation energy, which is defined as the energy needed to bring one mole of reactants from the ground state to the transition state of the reaction (Laidler, 1987a).

$$k_c = k_o e^{\left(-\frac{E_a}{RT}\right)} \qquad (1)$$

Solvent effects may be quantified using this relationship by determining the changes in activation energy that occur with changes in solvent properties (Hughes and Ingold, 1935, Tester, 1996). A solvent's effect on reaction rate is then discussed in terms of its ability to stabilize the transition state (Laidler, 1987b). Stabilization of the transition state through changes in solvent environment produces a lower energy of activation and a faster reaction. Prediction of solvent effects on reaction rates is accomplished through linear correlation of the log of the rate constant, which is proportional to the activation energy, versus an appropriate solvent property. Examples

of solvent properties against which correlations can be made include density, dielectric constant, or a solvatochromic parameter such as a, which measures a solvent's hydrogen bond donating ability; b, which measures hydrogen bond accepting ability; or p^*, which measures polarity/polarizability (Kim and Johnston, 1987a). A drawback of this method is that a large amount of experimental rate data needs to be collected in order to apply the technique. The data must cover a wide range of solvent types and reaction conditions before solvent effects can be predicted for an uncorrelated solvent. Even if the necessary data is available, the reaction rate predicted for the new solvent may possess significant error due to unusual specific interactions between solvent and reactants.

Transition State Theory

A more rigorous approach to the prediction of solvent effects on reaction rate is provided by transition state theory. In this treatment, it is assumed that the rate of reaction is dependent on an equilibrium established between the two reactant molecules and an "activated complex".

$$A + B \leftrightarrow M \leftrightarrow \text{Products}$$

The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities. (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

$$K_{eq} = \frac{[M]}{[A][B]} \frac{\gamma_M}{\gamma_A \gamma_B} \qquad (2)$$

Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

$$k = k_O \frac{\gamma_A \gamma_B}{\gamma_M} \tag{3}$$

In equation (3), the rate constant k is a product of k_o, the rate constant in a standard state environment (where all activities are unity), and the activity coefficients of the reactants and activated complex at the actual conditions of the reaction. This relationship cannot predict absolute reaction rates, but does have the potential to predict changes in the rate constant with a change in reaction conditions. The ability of this relationship to predict reaction rates relative to the rate at a standard state is limited only by the validity of the solution theory used to define the activity coefficients. If a solution theory possessing a small number of adjustable parameters is applicable to a given reaction, transition state theory has the potential to provide solvent effect predictions with less data than correlations based on Arrhenius activation energies.

Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, and so it can be used to provide a simple example of how (3) can be modified for practical application (Hildebrand and Scott, 1962); Hildebrand, 1964 #105]. In the Scatchard and Hildebrand model, a solubility parameter, d, is defined for the solvent and each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When d is related to the activity of a component, the following simple relationship results.

$$RT \ln \gamma_j = v_j \left(\delta_j - \overline{\delta} \right)^2 \tag{4}$$

$$\bar{\delta} \equiv \sum_{i}^{m} \Phi_i \delta_i \tag{5}$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\bar{\delta}$ is to an excellent approximation the solubility parameter of the solvent d_S.

$$\ln\left(\frac{k}{k_O}\right) = \frac{v_A(\delta_A - \delta_S)^2 + v_B(\delta_B - \delta_S)^2 - v_M(\delta_M - \delta_S)^2}{RT} \tag{6}$$

Local Density Enhancement

The rate predictive model based on regular solution theory would probably not work in the near critical region of a solvent, due to the tendency of a near critical solvent to exhibit densities in the vicinity of the reactants that are higher than the density of the bulk fluid. This local density enhancement represents a significant change in solvent properties unrelated to dispersion forces, and so the regular solution theory based model would fail to account for its effects.

Local density enhancement is brought about by short range solute-solvent interactions at solvent densities between 0.4 and 0.8 times the critical density (Brennecke, et al., 1990; Eckert and Knutson, 1993; Kim and Johnston, 1987b; Paulaitis and Alexander, 1987). Local density enhancement has the effect of creating local or "true" reactant concentrations which differ from the concentrations found in the bulk fluid.

Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and subsequently correcting measured rate constants for these enhancement effects (Kim and

Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO_2, for example, suggests that in at least some cases changes in the rate constant near the critical pressure may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories.

PROGRESS THIS QUARTER

COLLECTION OF KINETIC DATA

During this quarter, measurement of the density dependence of the kinetic rate constant for PTAD and anthracene in supercritical solvents was continued. Attention was focused on CO_2/cosolvent mixtures. Experiments were performed using binary mixtures of CO_2 and either chloroform or acetone as cosolvent. Cosolvent concentrations were varied between 0.00826 mol/L and 0.0826 mol/L. The cosolvents produced no significant change in the rate constant over that of pure CO_2 at these concentrations.

The rate constants for the reaction of PTAD with anthracene in supercritical CO_2 using acetone and chloroform as cosolvents are presented in Figure 1 and Figure 2. The cosolvent data is distributed on both sides of the pure CO2 data, which may indicate a lack of cosolvent effects at these concentrations.

PTAD can undergo rapid decomposition when heated in the presence of moderately protic solvents such as ethanol, but the decomposition was not considered to be a factor in these cosolvent experiments at the time that they were performed. This is because the time scale for decomposition at room temperature in liquid chloroform and liquid acetonitrile was on the order of days, while a given experiment generally did not last more than thirty minutes. These experimental results suggest that chloroform and acetonitrile may be more active in promoting decomposition in a supercritical medium at 40 °C than they were in the liquid phase at room temperature.

The lack of significant cosolvent effects on the rate is surprising - especially for experiments done using chloroform as the cosolvent. The reaction of PTAD with anthracene in liquid solvents showed significant sensitivity to changes in the nature of the

solvent. At 25 °C the rate constant in chloroform was greater than the rate constant in acetonitrile by a factor of 15. Since CO_2 is non-polar relative to acetonitrile and chloroform, the addition of a small amount of cosolvent was expected to produce an increase in rate constant.

Figure 1. Rate constants for the reaction of PTAD with anthracene at 40 °C in CO_2 and acetone.

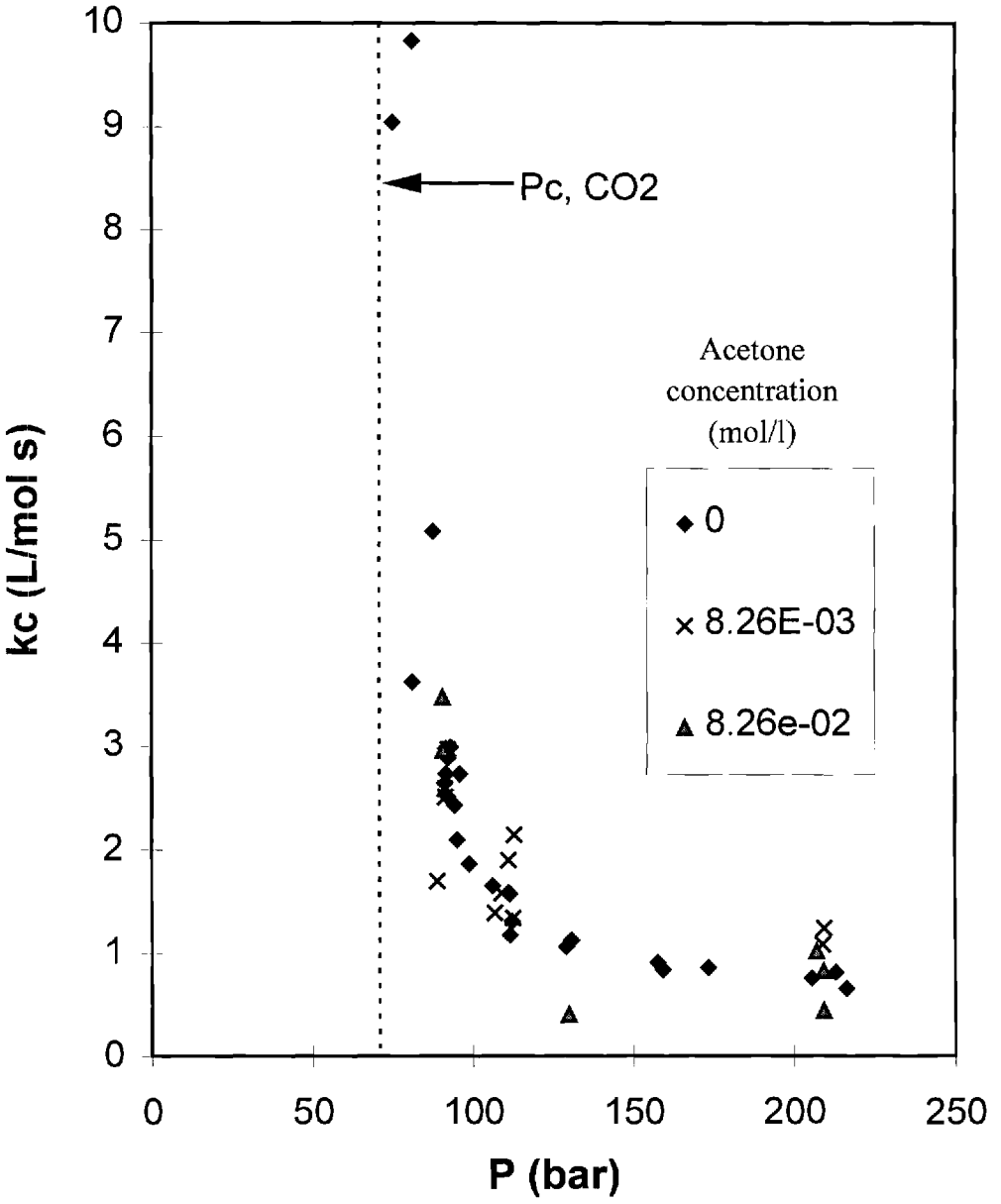
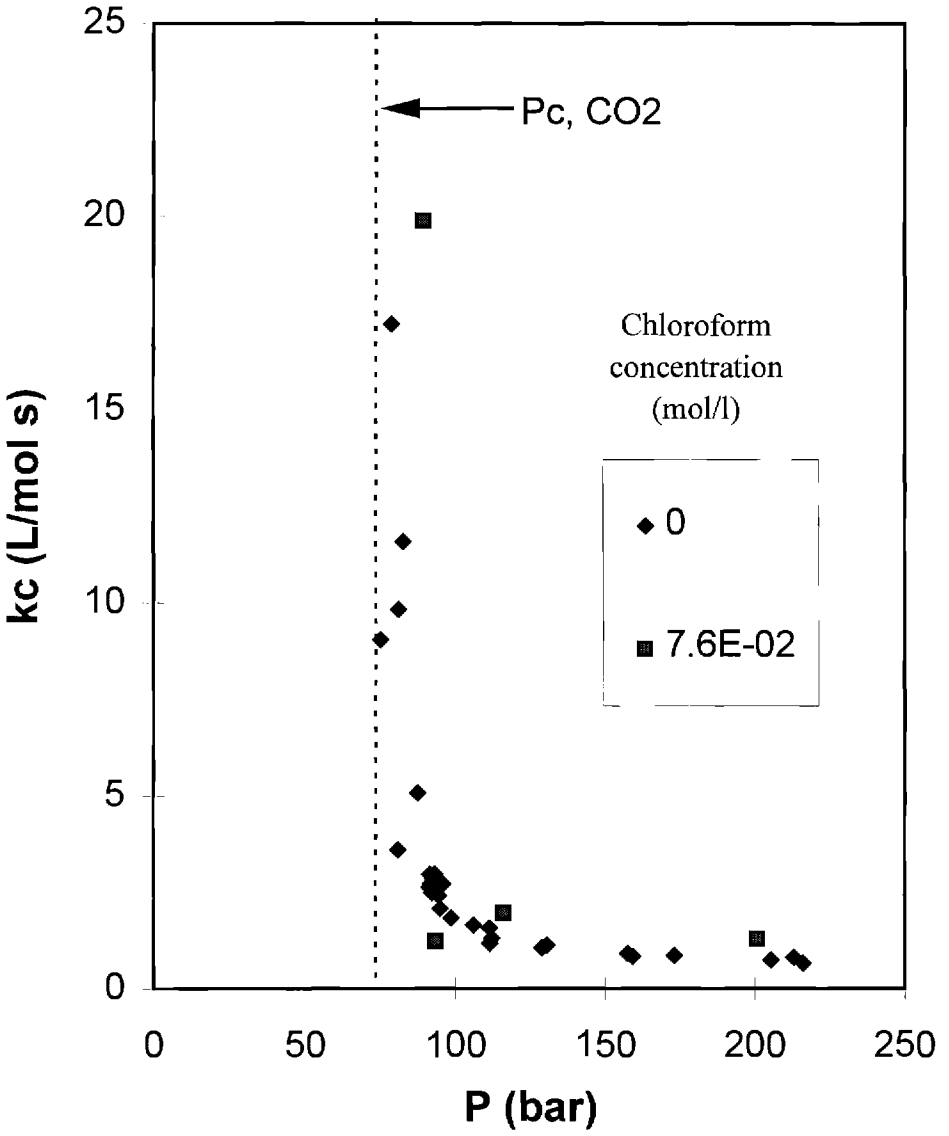


Figure 10. Rate constants for the reaction of PTAD with anthracene in CO_2 and chloroform. 40 °C



PLANS FOR NEXT QUARTER

KINETIC MEASUREMENTS

A second isotherm of kinetic data using pure CO_2 as the solvent will be collected in order to complete the data set necessary for modeling of the reaction kinetics in pure CO_2. A fit of the Arrhenius equation will be made with the assumption of constant activation energy versus density, and with the density dependence of the rate constant represented with a linear fit of the pre-exponential factor versus density. A model based on the Bronstead-Bjerrum relationship will also be applied, using fugacity coefficients with a high pressure reference state derived from the Peng-Robinson equation of state.

SUMMARY

Measurement of the density dependence of the kinetic rate constant for PTAD and anthracene in supercritical solvents was continued. Having completed studies of rates versus density in pure CO_2 at 40 °C, attention was focused on CO_2/cosolvent mixtures. Experiments were performed using binary mixtures of CO_2 and either chloroform or acetone as cosolvent. Cosolvent concentrations were varied between 0.00826 mol/L and 0.0826 mol/L. The cosolvents produced no significant change in the rate constant for that of pure CO_2 at these concentrations.

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering
(404) 894-7070

Initiation Date: September 1, 1994

Period Covered by Report: January 1, 1997 - March 31, 1997

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels - Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

Kinetic data has been previously collected for pure CO2 at pressures between the critical pressure of CO2 (73.8 bar) and 216 bar. This data is now being used to construct mathematical forms which can model these pressure induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

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The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities. (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

$$K_{eq} = \frac{[M]}{[A][B]} \frac{\gamma_M}{\gamma_A \gamma_B} \qquad (2)$$

Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

$$k = k_O \frac{\gamma A \gamma B}{\gamma M} \qquad (3)$$

In equation (3), the rate constant k is a product of k_o, the rate constant in a standard state environment (where all activities are unity), and the activity coefficients of the reactants and activated complex at the actual conditions of the reaction. This relationship cannot predict absolute reaction rates, but does have the potential to predict changes in the rate constant with a change in reaction conditions. The ability of this relationship to predict reaction rates relative to the rate at a standard state is limited only by the validity of the solution theory used to define the activity coefficients. If a solution theory possessing a small number of adjustable parameters is applicable to a given reaction, transition state theory has the potential to provide solvent effect predictions with less data than correlations based on Arrhenius activation energies.

Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, and so it can be used to pro[illegible] (3) can be modified for [illegible] application (Hildebrand and Scott, 1962); Hildebrand, 1964 #105]. In the Scatchard and Hildebrand model, a solubility parameter, d, is defined for the solvent and each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When d is related to the activity of a component, the following simple relationship results.

$$RT \ln \gamma_j = v_j \left(\delta_j - \overline{\delta} \right)^2 \qquad (4)$$

$$\bar{\delta} \equiv \sum_{i}^{m} \Phi_i \delta_i \qquad (5)$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\bar{\delta}$ is to an excellent approximation the solubility parameter of the solvent d_S.

$$\ln\left(\frac{k}{k_O}\right) = \frac{v_A(\delta_A - \delta_S)^2 + v_B(\delta_B - \delta_S)^2 - v_M(\delta_M - \delta_S)^2}{RT} \qquad (6)$$

Local Density Enhancement

The rate predictive model based on regular solution theory would probably not work in the near critical region of a solvent, due to the tendency of a near critical solvent to exhibit densities in the vicinity of the reactants that are higher than the density of the bulk fluid. This local density enhancement represents a significant change in solvent properties unrelated to dispersion forces, and so the regular solution theory based model would fail to account for its effects.

Local density enhancement is brought about by short range solute-solvent interactions at solvent densities between 0.4 and 0.8 times the critical density (Brennecke, et al., 1990; Eckert and Knutson, 1993; Kim and Johnston, 1987b; Paulaitis and Alexander, 1987). Local density enhancement has the effect of creating local or "true" reactant concentrations which differ from the concentrations found in the bulk fluid.

Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and subsequently correcting measured rate constants for these enhancement effects (Kim and

Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO_2, for example, suggests that in at least some cases changes in the rate constant near the critical pressure may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories.

PROGRESS THIS QUARTER

Modeling of Kinetic Data in Pure Supercritical CO_2

Rate constants were previously obtained for the reaction in pure CO_2 at 40 °C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 216 bar. Rate constant values are plotted in Figures 1 and 2. Two views are provided for the purpose of making the cluster of points at 95 bar more readable. The reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are as much as 26 times greater than those above 110 bar. The average estimated error in rate constant values was 20% at higher pressures, increasing to as much as 70% near the critical pressure.

The drop in rate constant with increasing pressure are similar to results obtained for the esterification of phthalic anhydride with methanol in supercritical CO_2 [Brennecke, et al., 1994]. The bi-molecular rate constant for the phthalic anhydride reaction also decreased at pressures above the critical pressure, and produced rate constant enhancements near the critical pressure similar in magnitude to those observed for the PTAD reaction. Brennecke estimated the local concentration of methanol around a phthalic anhydride molecule using an analogy with solvatochromic work using phenol-blue [Johnston, 1987 #58]. She determined that in the region near the critical pressure local concentration was higher than bulk concentrations by a factor of 5. When this increase in local concentration was accounted for, and rate constants were calculated using local concentration values, the reaction showed only a slight sensitivity to pressure in the region near the critical pressure.

Figure 1. The rate constants for the reaction of PTAD with anthracene in pure CO_2 at 40 °C.

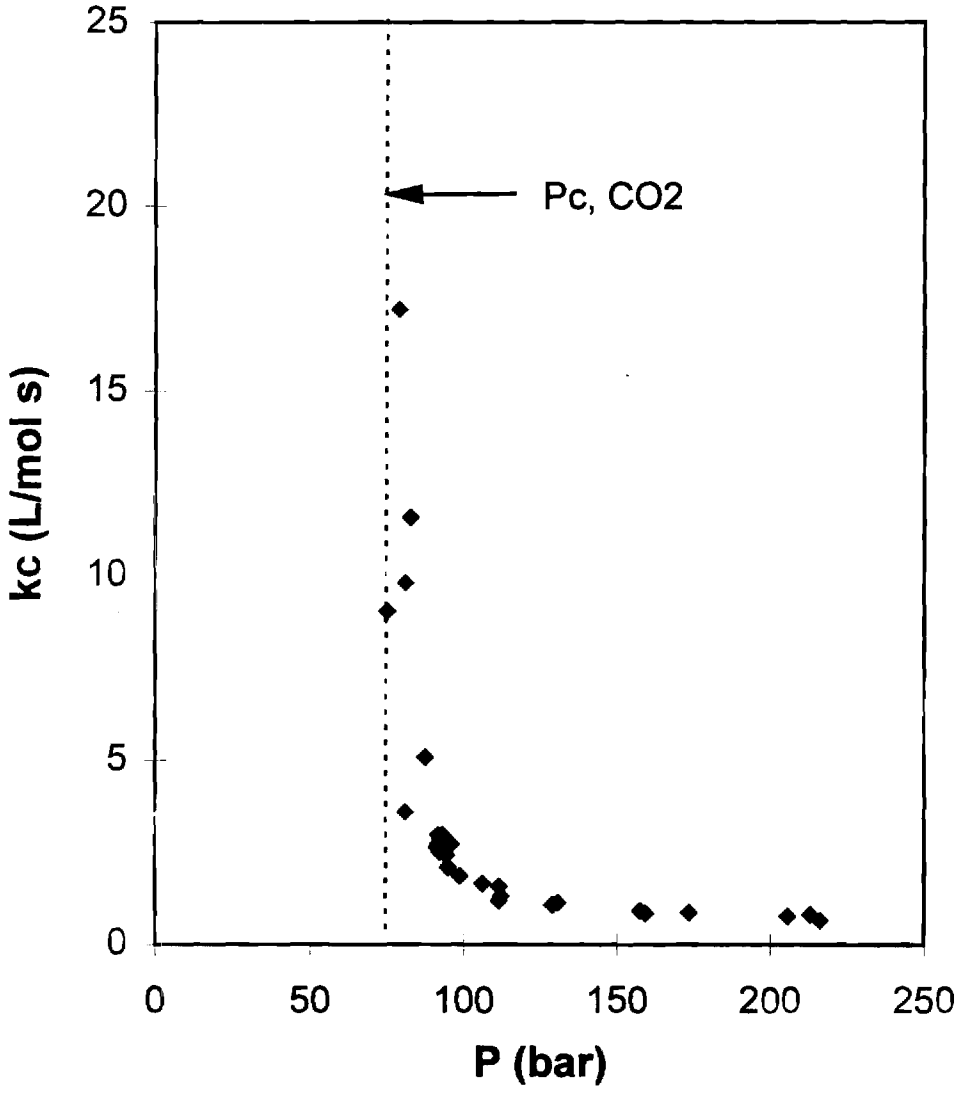
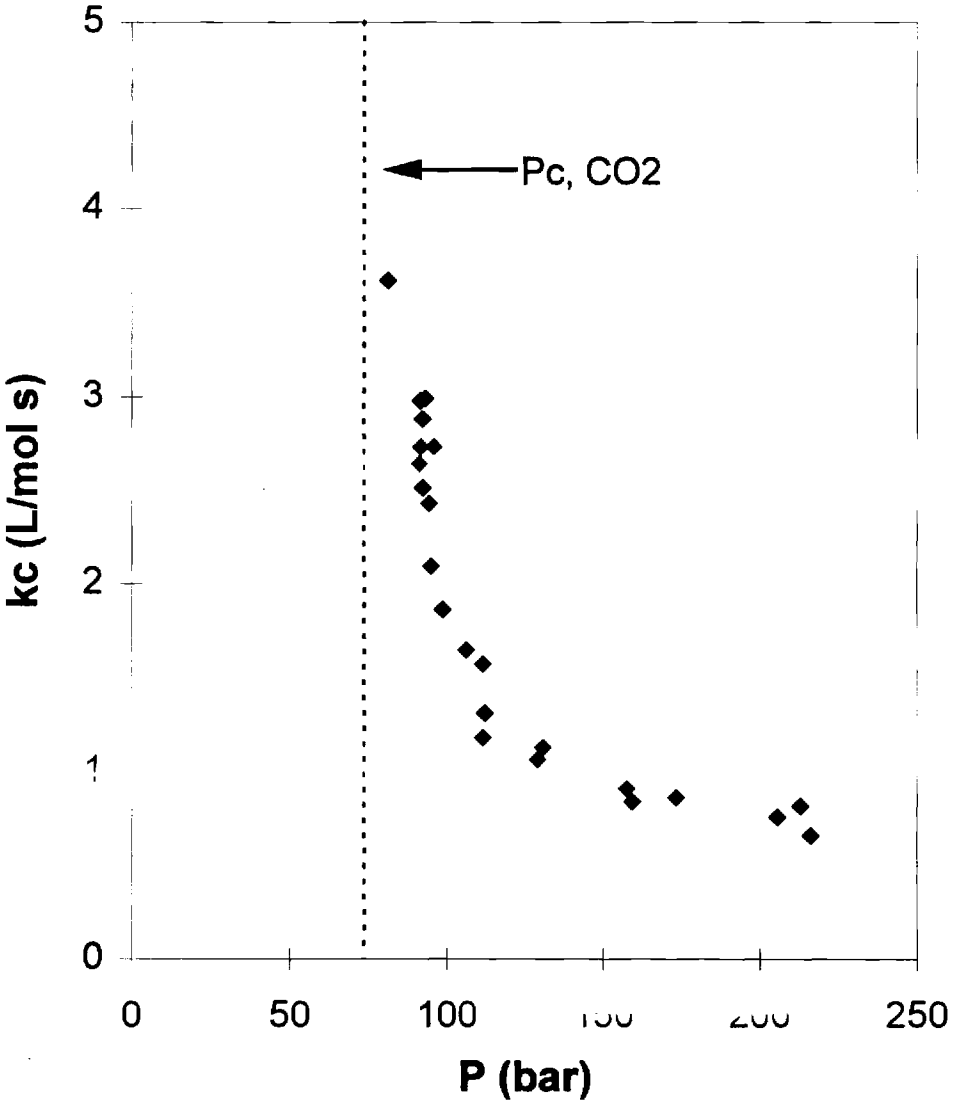


Figure 2. Rate constants having values less than 5 l/mol s for the reaction of PTAD with anthracene in pure CO_2 at 40 °C.



In order for a local concentration increase to occur in the reaction of PTAD with anthracene, it would be necessary for solute-solute clustering to be present along with solute-solvent clustering. Evidence for solute-solute clustering in dilute solutions is found in work by Kurnik [Kurnik, 1982 #98], so clustering effects on local concentrations are one possible explanation of the rate constant trends found in this work.

The construction of mathematical models capable of predicting these kinetic changes is now underway. The simplest promising avenue of investigation involves the assumption that the clustering effects are minimal, and that the kinetics may be successfully modeled as a function of changes in bulk fluid properties. The supercritical CO_2 can then be treated as a dense gas, which allows the following kinetic model based on high reference pressure fugacity coefficients to be derived (Eckert, 1974).

$$\frac{k}{k_o} = \frac{\phi_A \phi_B z}{\phi_M} \qquad (7)$$

Here, $\phi's$ are fugacity coefficients, and z is the usual compressibility factor of the gaseous mixture. Currently, a computer program for evaluating these fugacity coefficients at arbitrary pressures is being written. Evaluation of the fugacity coefficient model against experimental data using this program will continue into the next quarter.

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DOE F 1332.7 (8-89) EFG (07-90)

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QUARTERLY PROGRESS REPORT

SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

Project No. E-19-X50
Contract No. DE-FG22-94PC94206

Principal Investigator: Professor Charles A. Eckert
Georgia Institute of Technology
School of Chemical Engineering &
Specialty Separations Center
(404) 894-7070

Initiation Date: September 1, 1994

Period Covered by Report: April 1, 1997 – June 30, 1997

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we propose to develop a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The Diels – Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was chosen as the model system and was investigated in supercritical carbon dioxide.

Kinetic data have been previously collected for pure CO_2 at 40°C and pressures between the critical pressure of CO_2 (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are currently reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

The data taken at 40°C are now being used to construct mathematical forms which can model these pressure-induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

OBJECTIVES

The goal of this work is to design benign solvent/cosolvent systems for reactions which will achieve optimum desulfurization and/or denitrogenation in the pre-treatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of sulfur and nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general [Brennecke, 1989; Ekart, 1991; Johnston, 1989], as well as in many specific applications to environmental control [Eckert, 1986; Leman, 1990].

The specific objectives of this work are three fold. The first objective is the quantification of the intermolecular interactions affecting reaction transition states in SCFs via kinetic measurements using well-characterized Diels-Alder reactions. The second objective is the characterization of the thermodynamics of the reacting systems. From the thermodynamics of the reacting species, detailed information about the transition state may be determined. The third objective is the development of molecular level mathematical models using the results from the first two objectives. The models

shall be developed using both an equation of state approach and linear solvation energy relationships with solvatochromic parameters.

INTRODUCTION

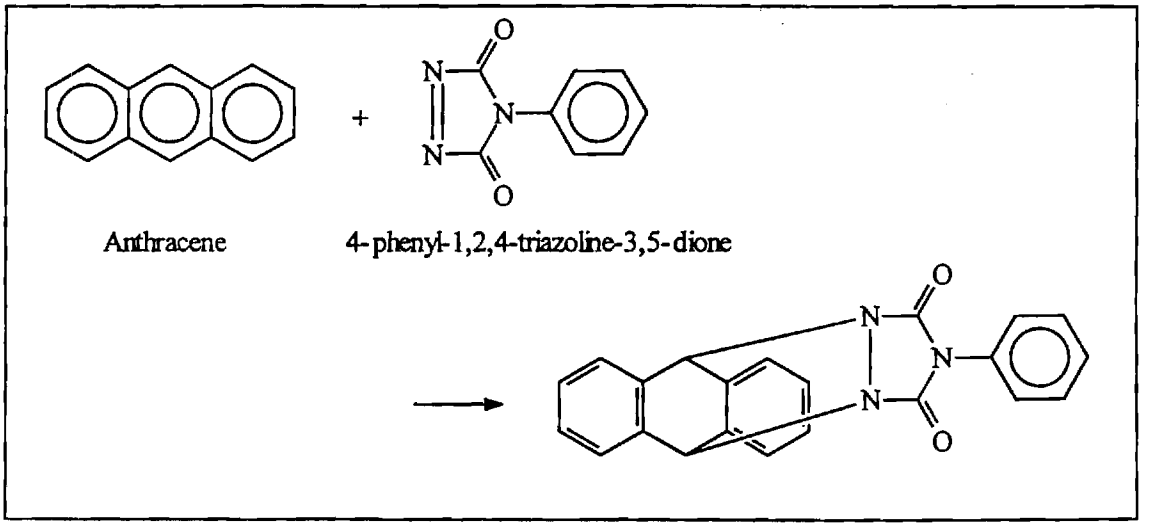
Over the last two decades, supercritical fluids have received an increasing amount of attention as a medium for carrying out chemical reactions (Savage, et al., 1995). The interest stems from unique advantages that supercritical fluids provide in the area of reaction rate control. A supercritical fluid, defined as a material at conditions above its critical temperature and pressure, is highly compressible at conditions near its critical point. The compressibility of the solvent can lead to large changes in reaction rate over small changes in pressure, and since pressure can be manipulated easily and precisely, pressure tuning represents a convenient route to rate control. Additional control of reaction rate can often be achieved through modification of the supercritical solvent with small amounts of a second solvent, designated as a cosolvent.

Among supercritical solvents, CO_2 has received special attention due to the fact that, in addition to a density which can easily be tuned over an order of magnitude, it also provides a compelling combination of low cost, an easily accessible, thermally mild critical point, and low toxicity. This combination of attributes is especially attractive to the food and pharmaceutical industries.

The reactants used to produce the rate data in this work follow a Diels-Alder reaction pathway, but the dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), is atypical. The reactive part of PTAD's structure is identical to maleimide, but has a pair of nitrogens at the bonding site instead of carbons. The reaction is illustrated in Figure 1. The nitrogen substitution results in reaction rates an order of magnitude higher than maleimide (Konovalov, et al., 1979), and has allowed the data presented in this work to

be collected relatively swiftly. PTAD possesses another attractive aspect in addition to its high reactivity, and that is the fact that, as a member of the Diels-Alder class of reactions, it is an elementary, bimolecular reaction with a well established mechanism (Sauer, 1967). This allows the rate constant to be measured using simple pseudo first order data reduction techniques.

Figure 1. The Diels-Alder reaction of anthracene (diene) with 4-phenyl-1,2,4-triazoline-3,5-dione (dienophile.)



BACKGROUND

A great deal of theoretical work has been done toward rate predictive models capable of correlating rate constant data versus various solvent properties and thermodynamic variables. A review of this broad field of research is beyond the scope of this work, but a thorough discussion is provided in reviews by Savage and Clifford (Clifford and Bartle, 1996; Savage, et al., 1995). For the present purpose, an overview of the most important concepts will suffice as an introduction to ways in which the data in this work could be employed in future modeling efforts.

Arrhenius Activation Energy

The most traditional method of analyzing rate data is in terms of the Arrhenius equation, which is presented as equation (1). The Arrhenius equation represents the exponential relationship between rate constant and temperature, and can be used to extract information on the activation energy, which is defined as the energy needed to bring one mole of reactants from the ground state to the transition state of the reaction (Laidler, 1987a).

$$k_c = k_o e^{\left(-\frac{E_a}{RT}\right)} \qquad (1)$$

Solvent effects may be quantified using this relationship by determining the changes in activation energy that occur with changes in solvent properties (Hughes and Ingold, 1935, Tester, 1996). A solvent's effect on reaction rate is then discussed in terms

of its ability to stabilize the transition state (Laidler, 1987b). Stabilization of the transition state through changes in solvent environment produces a lower energy of activation and a faster reaction. Prediction of solvent effects on reaction rates is accomplished through a linear correlation of the log of the rate constant, which is proportional to the activation energy, versus an appropriate solvent property. Examples of solvent properties against which correlations can be made include density, dielectric constant, or a solvatochromic parameter such as α, which measures a solvent's hydrogen bond donating ability; β, which measures hydrogen bond accepting ability; or π^*, which measures polarity/polarizability (Kim and Johnston, 1987a). A drawback of this method is that a large amount of experimental rate data needs to be collected in order to apply the technique. The data must cover a wide range of solvent types and reaction conditions before solvent effects can be predicted for an uncorrelated solvent. Even if the necessary data are available, the reaction rate predicted for the new solvent may possess significant error due to unusual specific interactions between solvent and reactants.

Transition State Theory

A more rigorous approach to the prediction of solvent effects on reaction rate is provided by transition state theory. In this treatment, it is assumed that the rate of reaction is dependent on an equilibrium established between the two reactant molecules and an "activated complex".

$$A + B \leftrightarrow M \leftrightarrow \text{Products}$$

The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

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Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

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Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, so it can be used to provide a simple example of how (3) can be modified for practical application (Hildebrand and Scott, 1962; Hildebrand, 1964 #105). In the Scatchard and Hildebrand model, a solubility parameter, δ, is defined for the solvent and for each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When δ is related to the activity of a component, the following simple relationship results.

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$$\bar{\delta} \equiv \sum_i^m \Phi_i \delta_i \qquad (5)$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\bar{\delta}$ is approximately equal to the solubility parameter of the solvent δ_S.

$$\ln\left(\frac{k}{k_O}\right) = \frac{v_A(\delta_A - \delta_S)^2 + v_B(\delta_B - \delta_S)^2 - v_M(\delta_M - \delta_S)^2}{RT} \qquad (6)$$

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Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and

subsequently correcting measured rate constants for these enhancement effects (Kim and Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO_2, for example, suggests that, in at least some cases, changes in the rate constant near the critical pressure may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories.

PROCEDURES

Fluorescence apparatus

Reaction kinetics were followed spectroscopically by fluorescence. The equipment used to make these measurements was configured in the manner illustrated in Figure 2. Light from a Spectral Energy SX1000-2 Xenon UV lamp was passed through a Kratos Analytical Model GM252 monochromator, producing an excitation light beam at a single wavelength. The excitation beam was split into two beams using a half-silvered mirror, producing an excitation beam and a reference beam.

The reference beam was directed into a Kratos D 500 Side-On Photomultiplier Tube (PMT), which produced an amperage output measured using a Keithley Instruments 414A Picoammeter. The excitation beam was directed into the optical cell containing the experimental sample of anthracene. The fluorescence of anthracene produced an emission beam of light, which was directed into a second GM252 monochromator where it was filtered to a single wavelength of light. The filtered emission wavelength was directed into a second D 500 PMT, which produced an amperage output that was measured using a Keithley 485 Autoranging Picoammeter.

Each picoammeter produced an analog output voltage in proportion to beam intensity, designated as Signal A for the emission beam intensity and as Signal B for the reference beam intensity. The ratio of these two signals - A/B - varied with changes in

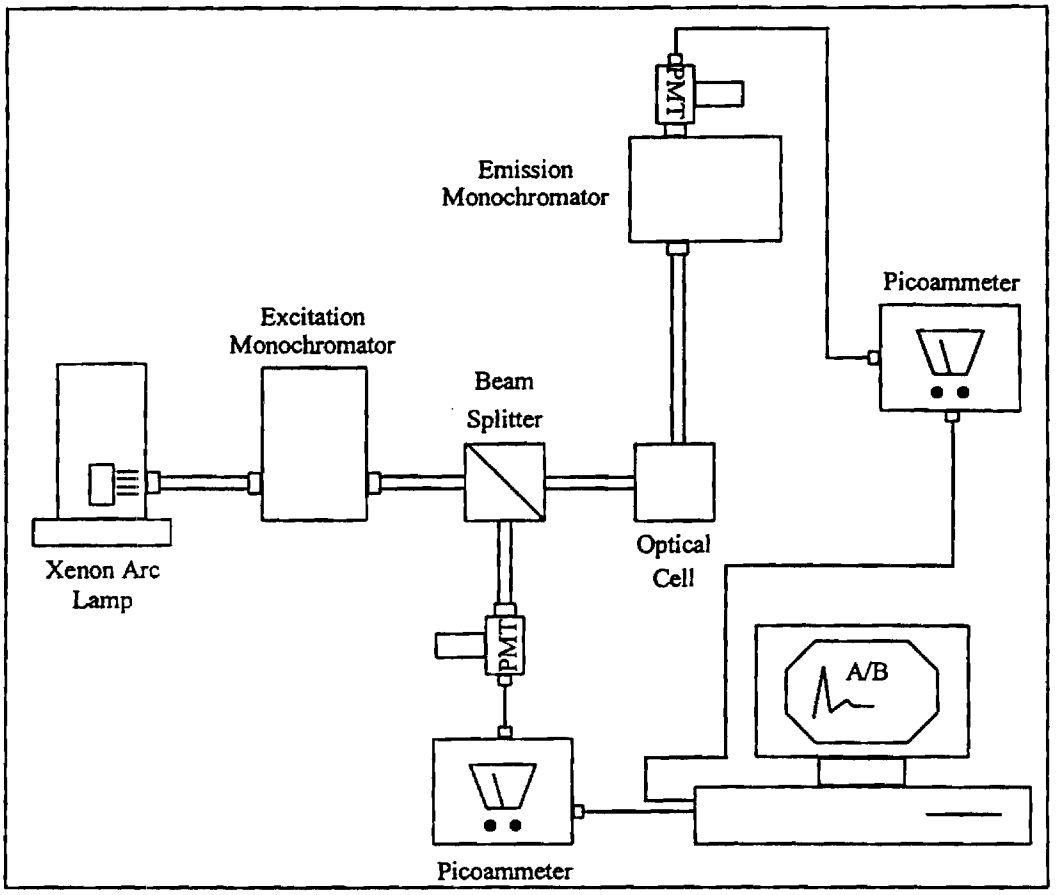


Figure 2. An overview of the high pressure fluorescence apparatus used for kinetic measurements.

fluorescent emission intensity, but it did not vary with fluctuations in lamp intensity. The emission intensity of the sample was recorded as the numerical value of the ratio A/B.

The optical cell was constructed from 316 stainless steel and was configured for solvent introduction and removal as in Figure 3. The windows were made from quartz, and were positioned at right angles to one another so that as little of the excitation light as possible would exit the cell with the emission light. The seals for cell windows were o-rings made of Teflon. All tubing and fittings were stainless steel and were manufactured by Swagelok or HiP. CO_2 was delivered to the cell using an ISCO Model 260D syringe pump, which fed through a Valco 6-port sample injection valve. A Teflon coated stirbar was used to provide agitation of the cell contents.

Pressure was measured using a Druck PDCR 911 transducer attached to a Druck DPI 60 digital readout. The pressure transducer and readout were calibrated using a Ruska dead weight calibration apparatus, and were found to be accurate to +/- 1 psi.

Internal temperatures were measured using a 1/16" grounded Omega Type K thermocouple in an inconel sheath. It was mounted with its tip in direct contact with the reactant solution. The thermocouple was attached to a readout with resolution to 0.1°C. The thermocouple was calibrated against a platinum resistance thermometer, and was found to be accurate to +/- 0.1°C.

Internal temperature was controlled using a second 1/8" Type K thermocouple mounted with its tip in the steel of the cellblock. The thermocouple was attached to an Omega CN9000A controller which used four cartridge heaters mounted in the steel of the cell block to maintain cell temperature. Temperature control of cell contents was within +/- 0.2°C.

Kinetic Analysis

The reaction of PTAD with anthracene is an elementary bimolecular reaction, so, if one reactant is present in excess, pseudo first order kinetics can be used to extract rate constants from concentration versus time data. UV spectroscopy was used for the analysis of the reaction rate of PTAD and anthracene in liquid solvents (Konovalov, Breus et al. 1979) by following the decay of PTAD over time. In order to apply pseudo first order kinetics, anthracene needs to be present in excess. Though an excess of anthracene is possible in liquids, PTAD solubility in supercritical CO_2 is on the order of 10^{-3} mol/L, and anthracene solubility is on the order of only 10^{-5} mol/L. The dilemma was solved by using fluorescence spectroscopy instead of UV. Fluorescence spectroscopy can detect concentrations of anthracene as low as 10^{-7} mol/L, making it possible to have PTAD present at an initial excess of 100:1 and still follow a change in anthracene concentration over two orders of magnitude.

In order to calculate the rate constant of the reaction conveniently from fluorescence emission data, it was possible to use Beer's law to relate pseudo first order rate constants directly to changes in emission signal. Solution of the differential equation (9) relating concentration changes of one reactant to the concentration of both reactants leads to (10) when PTAD is assumed to be in great excess and therefore constant throughout the reaction.

$$\frac{dc_{AN}}{dt} = k_c c_{PTAD} c_{AN} \qquad (9)$$

$$\ln\left(\frac{C_{AN}}{C_{ANo}}\right) = -\left(k_c C_{PTADo}\right)t \quad (10)$$

Simple experiments involving incremental additions of anthracene to a liquid solvent indicated that the fluorescence of anthracene follows Beer's Law (11) as long as the anthracene is dilute (i.e. less than 10^{-5} mol/l), and the emission wavelength monitored is well removed from wavelengths at which self-absorption may occur. The path length "l" in Beer's Law does not change during a run, so (11) may be written once for initial conditions and again for an arbitrary time t. The ratio of these equations may be substituted into (10), leading to (12). Equation (12) allows the pseudo first order rate constant to be derived directly from emission data without knowing the exact concentration of anthracene in the cell.

$$e = \varepsilon l c_{AN} \qquad (11)$$

$$\ln\left(\frac{e_{AN}}{e_{ANo}}\right) = -k_c c_{PTADo} t \qquad (12)$$

Kinetic Measurements in Pure Supercritical CO_2

Stock solutions of PTAD and anthracene were prepared in acetone. A fresh PTAD stock solution was prepared each day. A known quantity of each stock solution was placed into the optical cell using a Gilman Pipet, with PTAD in excess by a factor of 40. The cell was dried under vacuum for 5 minutes. Care was taken to insure that the two stock solutions did not contact one another during drying. Dryness of the cell was determined by visual inspection.

Data acquisition software was started, and the cell was pressurized with pure CO_2 from the ISCO syringe pump. The time and pressure at which the cell reached the desired temperature was recorded, and the reaction was observed for about twenty minutes. Kinetic analysis was performed only on data collected while the cell was at within +/- 0.2°C of the desired temperature. The cell was cleaned thoroughly with acetone between each experiment.

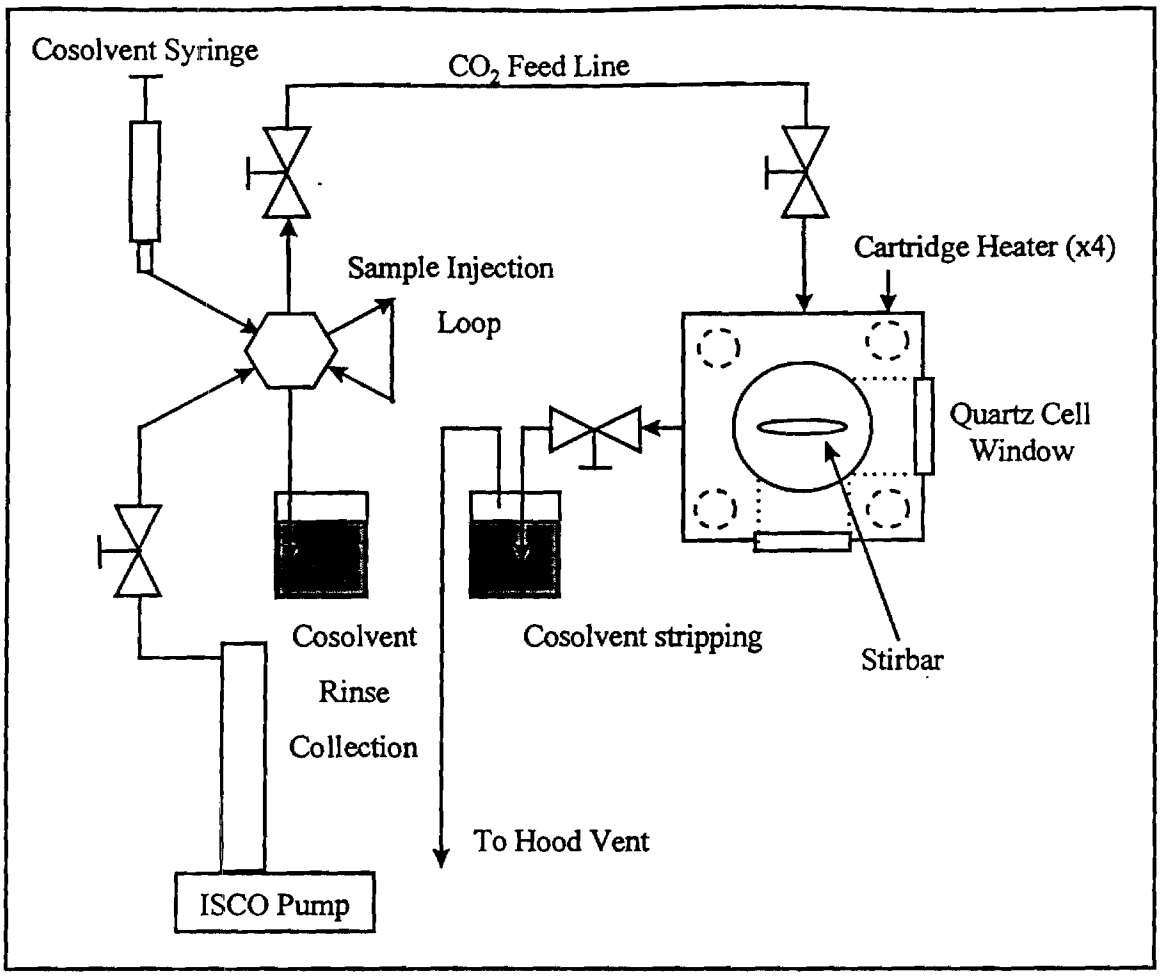


Figure 3. An overview of the optical cell and the apparatus used for the injection of cosolvents.

RESULTS AND DISCUSSION

Modeling of Kinetic Data in Pure Supercritical CO_2

Rate constants were previously obtained for the reaction in pure CO_2 at 40°C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 216 bar. Rate constant values are plotted in Figures 4 and 5. Two views are provided for the purpose of making the cluster of points at 95 bar more readable. Near the critical temperature, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are as much as 26 times greater than those above 110 bar. The average estimated error in rate constant values was 20% at higher pressures, increasing to as much as 70% near the critical pressure.

The drop in rate constant with increasing pressure is similar to the result obtained for the esterification of phthalic anhydride with methanol in supercritical CO_2 [Brennecke, et al, 1994]. The bimolecular rate constant for the phthalic anhydride reaction also decreased at pressures above the critical pressure and produced rate constant enhancements near the critical pressure similar in magnitude to those observed for the PTAD reaction. Brennecke estimated the local concentration of methanol around a phthalic anhydride molecule using an analogy with solvatochromic work using phenol-blue [Johnston, 1987 #58]. She determined that, in the region near the critical pressure, local concentration was higher than bulk concentrations by a factor of 5. When this increase in local concentration was accounted for, and rate constants were calculated using local concentration values, the reaction showed only a slight sensitivity to pressure in the region near the critical pressure.

Figure 4. Rate constants for the reaction of PTAD with anthracene in pure CO_2 at 40°C.

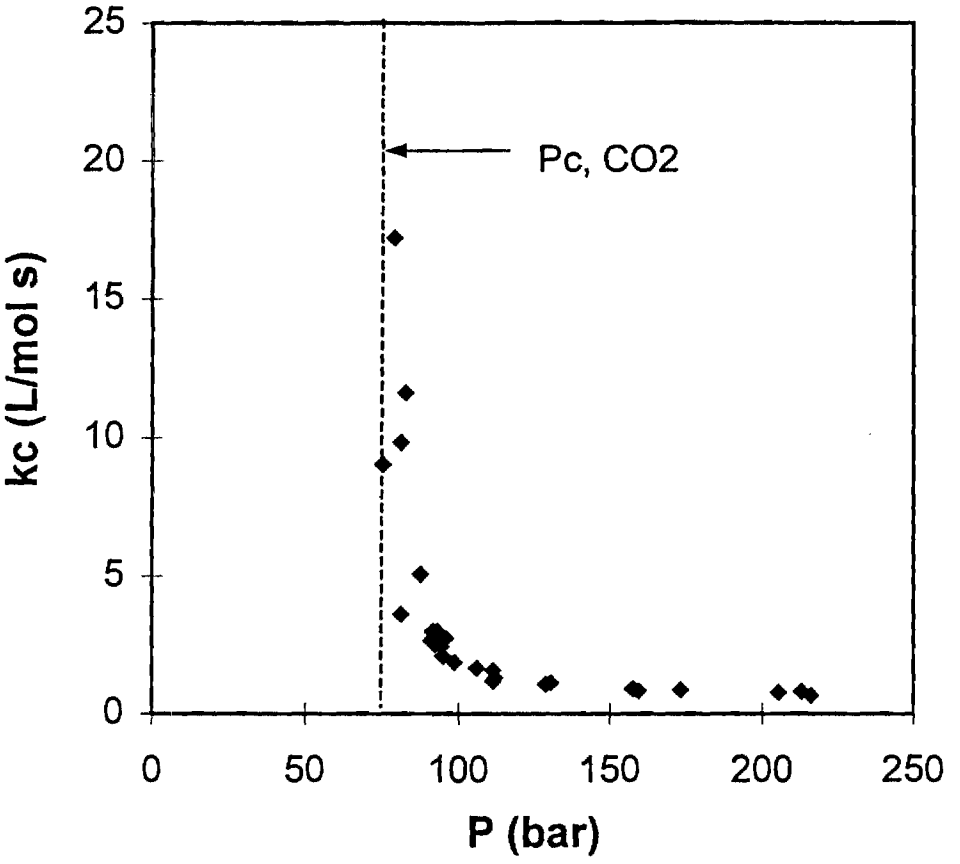
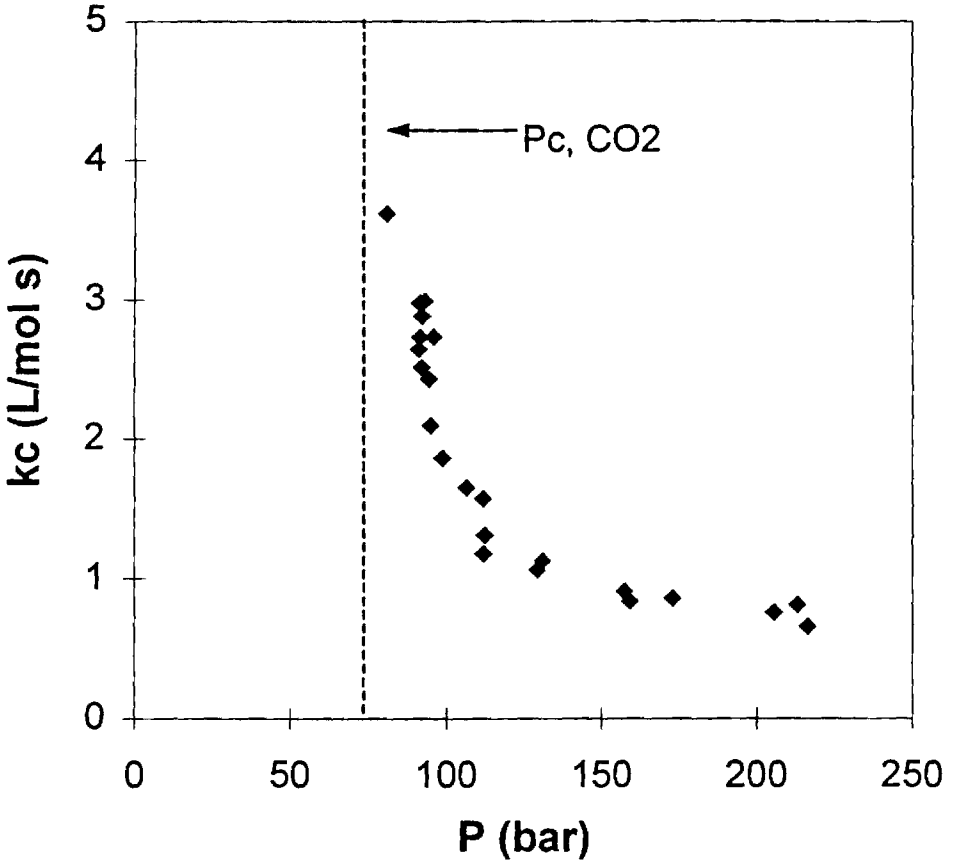


Figure 5. Rate constants having values less than 5 l/mol s for the reaction of PTAD with anthracene in pure CO_2 at 40°C.



In order for a local concentration increase to occur in the reaction of PTAD with anthracene, it is necessary for solute-solute clustering to be present along with solute-solvent clustering. Evidence for solute-solute clustering in dilute solutions is found in work by Kurnik [Kurnik, 1982 #98], so clustering effects on local concentrations are one possible explanation of the rate constant trends found in this work.

The construction of mathematical models capable of predicting these kinetic changes is now underway. The simplest promising avenue of investigation involves the assumption that the clustering effects are minimal, and that the kinetics may be successfully modeled as a function of changes in bulk fluid properties. The supercritical CO_2 can then be treated as a dense gas, which allows the following kinetic model based on high reference pressure fugacity coefficients to be derived (Eckert, 1974).

$$\frac{k}{k_o} = \frac{\phi_A \phi_B z}{\phi_M} \qquad (7)$$

Here, $\phi's$ are fugacity coefficients, and z is the usual compressibility factor of the gaseous mixture. Currently, a computer program for evaluating these fugacity coefficients at arbitrary pressures is being written. Evaluation of the fugacity coefficient model against experimental data using this program will continue into the next quarter.

Kinetic Data in Pure Supercritical CO_2 at 50°C

Rate constants were obtained for the reaction of PTAD with anthracene in pure CO_2 at 50°C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 195

bar. Rate constant values at both 40°C and 50°C are plotted in Figure 6. At 40°C, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are 25 times greater than those above 110 bar. At 50°C, the reaction rate constant shows only a slight change with pressure around the critical pressure. This slight increase in rate as pressure decreases is predicted by transition state theory (Evans and Polanyi, 1935; Brennecke, et al, 1994). The modest rate constants near the critical pressure indicate that molecular clustering is minimal at this temperature.

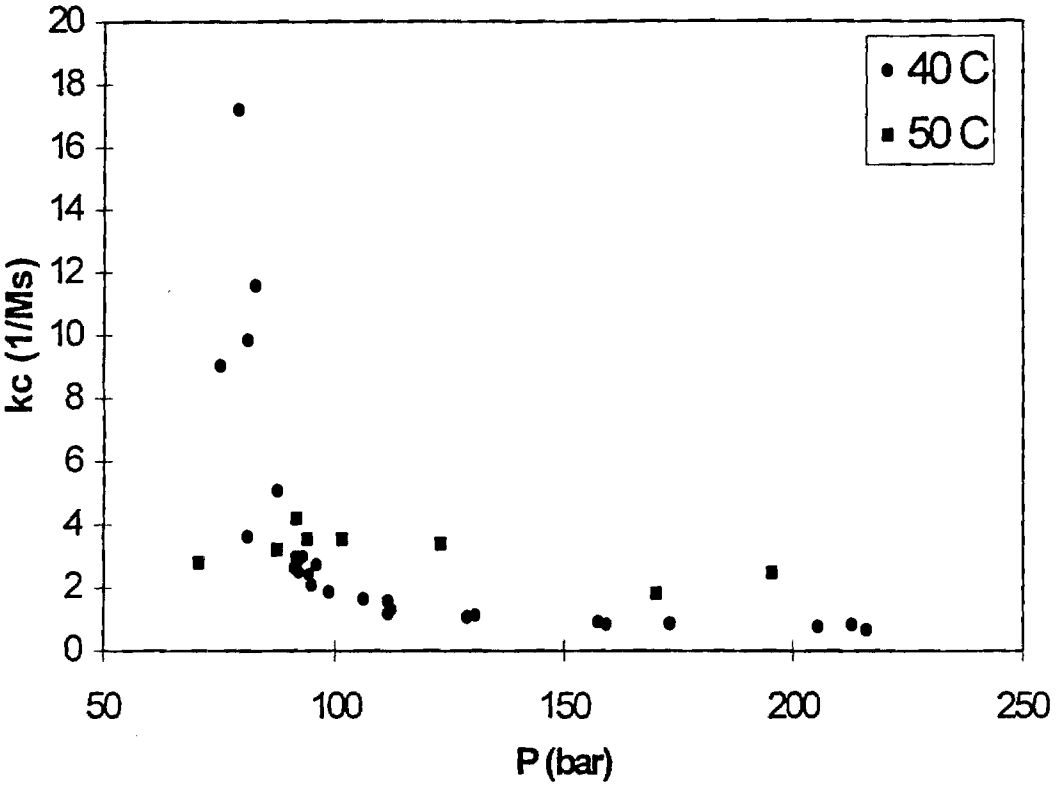


Figure 6. Rate constants for the reaction of PTAD with anthracene in pure CO_2 at 50°C.

CONCLUSION

Kinetic data have been previously collected for pure CO_2 at 40°C and pressures between the critical pressure of CO_2 (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are currently reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

The data taken at 40°C are now being used to construct mathematical forms which can model these pressure-induced kinetic changes. One promising avenue of investigation involves treating the supercritical medium as a dense gas, which allows a kinetic model based on high reference pressure fugacity coefficients to be derived.

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SUPERCRITICAL FLUID REACTIONS FOR COAL PROCESSING

FINAL TECHNICAL REPORT

Period Covered by Report: September 1, 1994 – August 31, 1997

Principal Investigator:
Professor Charles A. Eckert

Report Issued: November, 1997

DOE Award No.: DE-FG22-94PC94206

Submitting Organization:

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Atlanta, GA 30332-0100

DISCLAIMER

ABSTRACT

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we developed a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The tautomeric equilibrium of a Schiff base was chosen as one model system and was investigated in supercritical ethane and cosolvent modified supercritical ethane. The Diels-Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was selected as a second model system, and it was investigated in supercritical carbon dioxide.

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EXECUTIVE SUMMARY

Exciting opportunities exist for the application of supercritical fluid (SCF) reactions for the pre-treatment of coal. Utilizing reactants which resemble the organic nitrogen containing components of coal, we developed a method to tailor chemical reactions in supercritical fluid solvents for the specific application of coal denitrogenation. The tautomeric equilibrium of a Schiff base was chosen as one model system and was investigated in supercritical ethane and cosolvent modified supercritical ethane. The Diels-Alder reaction of anthracene and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) was selected as a second model system, and it was investigated in supercritical carbon dioxide.

INTRODUCTION

The goal of this work is to develop benign solvent/cosolvent systems for reactions which will achieve optimum denitrogenation in the pretreatment of coal or coal liquids. Supercritical fluids present excellent opportunities for the pre-treatment of coal, hence we shall utilize supercritical fluids as a reaction medium. A SCF exists in a single phase just above the critical temperature at elevated pressures. It has a liquid-like density, which gives a large capacity for solvation, and it has a high molecular diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer. Further, its high compressibility gives large density variations with very small pressure changes, yielding extraordinary selectivity characteristics, which are most important in the removal of nitrogen from coal or coal liquids. Significant work has already been carried out in such applications, both in general (Johnston, 1989; Ely, 1991; Brennecke, 1989), as well as in many specific applications to environmental control (Leman, 1990; Eckert, 1986).

There are four specific objectives of this work. First is the use of supercritical fluids and modified supercritical fluids to tune the chemical equilibria of model coal compounds. A second objective is to model the density dependence of the equilibrium constant using a chemical-physical approach. Third is the quantification of the intermolecular interactions affecting reaction transition states in SCFs via kinetic measurements using well-characterized Diels-Alder reactions. The final objective is the characterization of the thermodynamics of the reacting systems. From the

thermodynamics of the reacting species, detailed information about the transition state may be determined.

BACKGROUND

A great deal of theoretical work has been done toward rate predictive models capable of correlating rate constant data versus various solvent properties and thermodynamic variables. A review of this broad field of research is beyond the scope of this work, but a thorough discussion is provided in reviews by Savage and Clifford (Clifford and Bartle, 1996; Savage, et al., 1995). For the present purpose, an overview of the most important concepts will suffice as an introduction to ways in which the data in this work could be employed in future modeling efforts.

Arrhenius Activation Energy

The most traditional method of analyzing rate data is in terms of the Arrhenius equation, which is presented as equation (1). The Arrhenius equation represents the exponential relationship between rate constant and temperature, and can be used to extract information on the activation energy, which is defined as the energy needed to bring one mole of reactants from the ground state to the transition state of the reaction (Laidler, 1987a).

$$k_c = k_o e^{\left(-\frac{E_a}{RT}\right)} \qquad (1)$$

Solvent effects may be quantified using this relationship by determining the changes in activation energy that occur with changes in solvent properties (Hughes and

Ingold, 1935, Tester, 1996). A solvent's effect on reaction rate is then discussed in terms of its ability to stabilize the transition state (Laidler, 1987b). Stabilization of the transition state through changes in solvent environment produces a lower energy of activation and a faster reaction. Prediction of solvent effects on reaction rates is accomplished through a linear correlation of the log of the rate constant, which is proportional to the activation energy, versus an appropriate solvent property. Examples of solvent properties against which correlations can be made include density, dielectric constant, or a solvatochromic parameter such as α, which measures a solvent's hydrogen bond donating ability; β, which measures hydrogen bond accepting ability; or π^*, which measures polarity/polarizability (Kim and Johnston, 1987a). A drawback of this method is that a large amount of experimental rate data needs to be collected in order to apply the technique. The data must cover a wide range of solvent types and reaction conditions before solvent effects can be predicted for an uncorrelated solvent. Even if the necessary data are available, the reaction rate predicted for the new solvent may possess significant error due to unusual specific interactions between solvent and reactants.

Transition State Theory

A more rigorous approach to the prediction of solvent effects on reaction rate is provided by transition state theory. In this treatment, it is assumed that the rate of reaction is dependent on an equilibrium established between the two reactant molecules and an "activated complex".

$$A + B \leftrightarrow M \leftrightarrow \text{Products}$$

The activated complex M is formed from the association of two reactant molecules A and B as bonds are broken and formed on the way to product. Though the activated complex is unstable along the reaction coordinate, it is considered to be a normal molecule in equilibrium with the reactants and may therefore be used in writing relationships based on thermodynamic activities (Eckert, 1967; Evans and Polanyi, 1935; Eyring, 1935).

$$K_{eq} = \frac{[M]}{[A][B]} \frac{\gamma_M}{\gamma_A \gamma_B} \tag{2}$$

Equation (2) was related to chemical reaction rates by Bronsted and Bjerrum (Bjerrum, 1924; Bronsted, 1922), producing a general statement which relates the reaction rate constant to solvent effects through activity coefficients.

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_M} \tag{3}$$

In equation (3), the rate constant k is a product of k_o, the rate constant in a standard state environment (where all activities are unity), and the activity coefficients of the reactants and activated complex at the actual conditions of the reaction. This

relationship cannot predict absolute reaction rates, but does have the potential to predict changes in the rate constant with a change in reaction conditions. The ability of this relationship to predict reaction rates relative to the rate at a standard state is limited only by the validity of the solution theory used to define the activity coefficients. If a solution theory possessing a small number of adjustable parameters is applicable to a given reaction, transition state theory has the potential to provide solvent effect predictions with less data than correlations based on Arrhenius activation energies.

Scatchard and Hildebrand's regular solution theory estimates activity coefficients for an ideal system in which only dispersion forces need be considered, so it can be used to provide a simple example of how (3) can be modified for practical application (Hildebrand and Scott, 1962; Hildebrand, 1964 #105). In the Scatchard and Hildebrand model, a solubility parameter, δ, is defined for the solvent and for each reactant, based on the "cohesive energy density" of the material - an experimentally measurable value that represents the strength of dispersion forces as the energy needed to isothermally vaporize a given molar volume of liquid to the ideal gas state. When δ is related to the activity of a component, the following simple relationship results.

$$RT \ln \gamma_j = v_j \left(\delta_j - \bar{\delta} \right)^2 \qquad (4)$$

$$\overline{\delta} \equiv \sum_{i}^{m} \Phi_i \delta_i \tag{5}$$

Substitution into (3) leads to the following useful result. Note that for work done with dilute reactants, $\overline{\delta}$ is approximately equal to the solubility parameter of the solvent δ_S.

$$\ln\left(\frac{k}{k_O}\right) = \frac{v_A\left(\delta_A - \delta_S\right)^2 + v_B\left(\delta_B - \delta_S\right)^2 - v_M\left(\delta_M - \delta_S\right)^2}{RT} \tag{6}$$

Local Density Enhancement

The rate predictive model based on regular solution theory would probably not work in the near critical region of a solvent, due to the tendency of a near critical solvent to exhibit densities in the vicinity of the reactants that are higher than the density of the bulk fluid. This local density enhancement represents a significant change in solvent properties unrelated to dispersion forces, and the regular solution theory based model would fail to account for its effects.

Local density enhancement is brought about by short-range solute-solvent interactions at solvent densities between 0.4 and 0.8 times the critical density (Brennecke, et al., 1990; Eckert and Knutson, 1993; Kim and Johnston, 1987b; Paulaitis and Alexander, 1987). Local density enhancement has the effect of creating local or "true" reactant concentrations which differ from the concentrations found in the bulk fluid.

Local density enhancements have been investigated using a solvatochromic method which correlates shifts in the transition energy of spectroscopic absorption maxima to changes in density in the immediate vicinity of a probe molecule. This provides a means of measuring density enhancements in a supercritical solvent, and subsequently correcting measured rate constants for these enhancement effects (Kim and Johnston, 1987a). Application of this method to an esterification reaction in supercritical CO_2, for example, suggests that, in at least some cases, changes in the rate constant near the critical pressure may be explained largely by the effect of density enhancement on local concentration, rather than by physical or thermodynamic effects (Brennecke, et al., 1994).

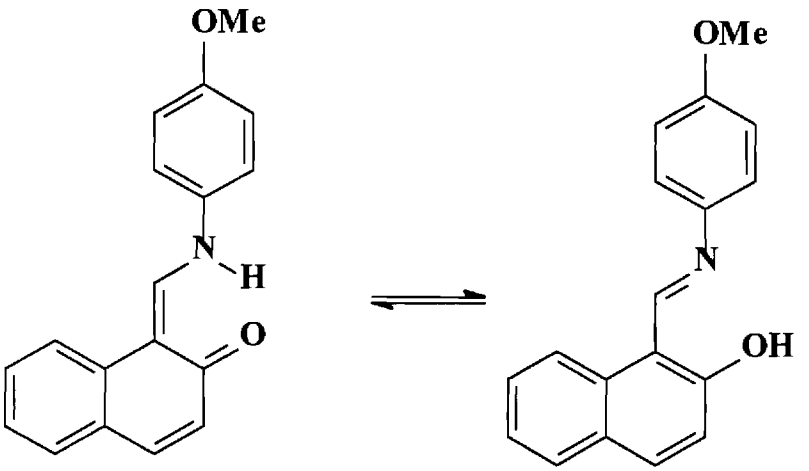
In conclusion, solvent characteristics peculiar to supercritical fluids, such as local density enhancement and high solvent compressibility near the critical point, present challenges to those who wish to develop predictive models of chemical reaction rates in supercritical solvents. A number of general theories capable of predicting solvent effects on reaction rates already exist. The challenge is to incorporate expressions which account for supercritical fluid solvent properties into these theories.

RESULTS AND DISCUSSION

I) TAUTOMERIC EQUILIBRIUM OF A SCHIFF BASE

Keto-Enol Equilibrium Measurements

Recent studies of chemical equilibria have focused on the effects of pressure on the equilibrium constants of solutes in pure supercritical fluids (Yagi, 1993; Kazarian, 1993; Yamasaki, 1990). The presence of a cosolvent complicates the system, especially if the cosolvent is capable of participating in specific interactions with the solute molecule and leads to multiple equilibria. However, it is the purpose of this study to quantify the effect of cosolvents on keto-enol equilibrium constant for the Schiff base, 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol (Figure 1), especially in the near-critical region where local composition enhancements are expected to have a large effect on the equilibrium constant.



KETO **ENOL**

Figure 1. Tautomeric equilibrium of the Schiff base 4-(methoxy)-1-(N-phenylforminidoyl)-2-naphthol.

The Schiff base and a blocked Schiff base (Figure 2) were synthesized by a condensation reaction of 2-hydroxynaphthaldehyde and p-methoxy aniline in ethanol (Salman, 1991) and by a condensation reaction of 2-methoxy-1-naphthaldehyde and 4-methoxyaniline in ethanol, respectively. Yellow solids of blocked Schiff base were obtained after filtration, washing twice with cold ethanol and drying under vacuum. ^{1}H NMR ($CDCL_3$ and TMS): δ = 3.78 ppm (s, 3H); 6.94 ppm (d, 2H); 7.18 ppm (d, 1H); 7.30 ppm (d, 2H); 7.36 ppm (m, 1H); 7.56 ppm (m, 1H); 7.74 ppm (d,1H); 7.85 ppm (d, 1H); 9.25 ppm (s, 1H); 9.53 ppm (d, 1H); 13C NMR ($CDCl_3$ and TMS): δ = 55.30 ppm (s); 56.26 ppm (s); 112.53 ppm (s); 114.38 ppm (s); 117.37 ppm (s); 122.30 ppm (s); 124.23 ppm (s); 126.07 ppm (s); 128.29 ppm (s); 128.40 ppm (s); 129.26 ppm (s); 132.05

ppm (s); 133.39 ppm (s); 146.61 ppm (s); 157.02 ppm (s); 158.22 ppm (s); 159.31 ppm (s). The blocked Schiff base had the phenolic oxygen methylated to prohibit tautomerization so that the extinction coefficients of the enol form of the Schiff could be measured.

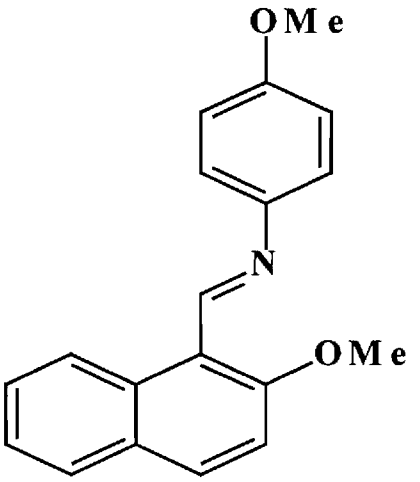


Figure 2. Blocked Schiff base.

Apparatus

A schematic of the modified UV spectrophotometer (Perkin Elmer 554) is shown in Figure 3. Single beam spectroscopy was used in this double beam apparatus using air as a constant background for enhanced signal to noise ratio. The spectrophotometer was modified to accommodate a stainless steel high pressure cell (Tomasko, 1992) with quartz windows (Heraeus Amersil). The path length of the cell was 0.75 cm and the volume was 5.88 ml The cell was stirred continuously using a mini stir plate (Variomag) and a stir bar (Fisher) placed inside the cell.

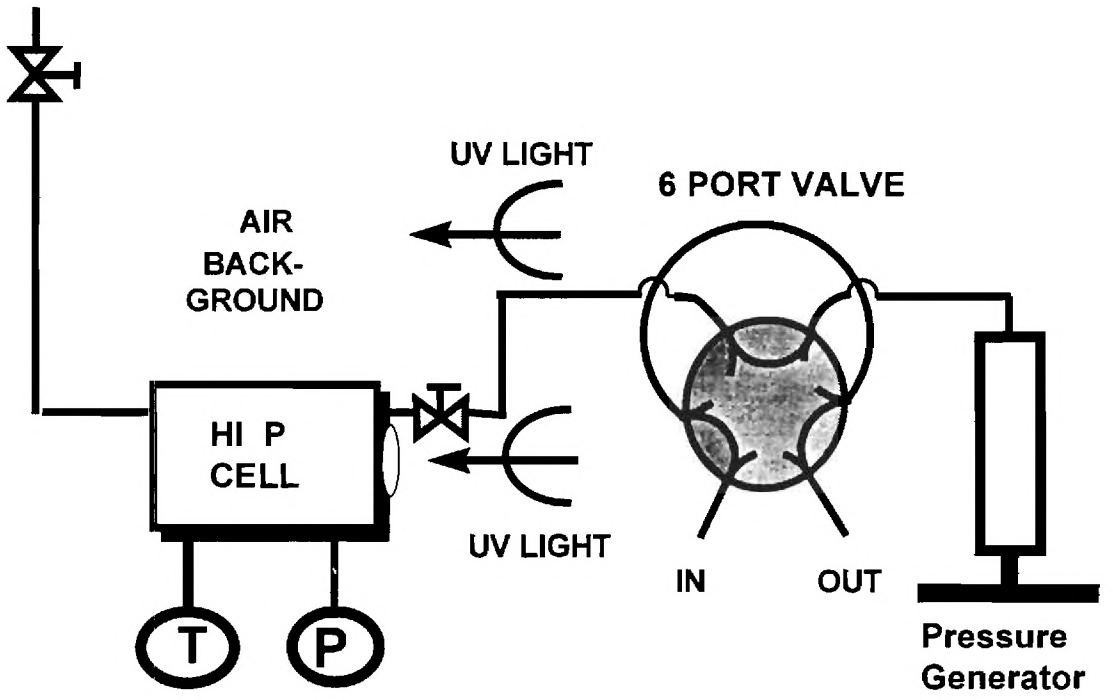


Figure 3. Schematic diagram of high pressure UV-Vis reaction apparatus.

The temperature inside the cell was monitored with an internal thermistor (Omega, calibrated within ± 0.1°C) and controlled manually using an EPSCO DC power supply (Model D-612T). Heat was supplied by thermoelectric heaters (Melcor). The pressure was controlled using a 60 cm^3 piston type high pressure generator (High Pressure Equipment, Model 87-6-5) and measured to within ± 2 psi with a Heise digital pressure gauge (Model 901B). A Valco 6-port sampling valve with external sample loops ranging in size from 20-100 l was used to inject cosolvent directly into the high pressure cell.

Procedure

Single beam spectroscopy was used to monitor absorbance as a function of increasing pressure at constant probe and cosolvent concentrations. All measurements were made at a constant temperature of 35°C (± 0.1°C), and all experiments were carried out in the single phase region, as confirmed by separate miscibility experiments (Yun, 1996) (Table 1).

Table 1. Pressure limits of miscibility for SCF ethane/cosolvent mixtures.

Cosolvent in SCF Ethane	Cosolvent Concentration (mol/L)	Lower Miscibility Limit (psig)
Trifluoroethanol	0.24	800
Trifluoroethanol	0.12	756
Trifluoroethanol	0.046	738
Hexafluoroiso-propanol	0.32	721
Hexafluoroiso-propanol	0.16	713
Hexafluoroiso-propanol	0.08	Miscible at all conditions observed.
Ethanol	0.2	Miscible at all conditions observed.
Ethanol	0.1	Miscible at all conditions observed.

Spectra at different pressures were recorded, starting with a low pressure as determined by the miscibility limit, and incrementally going to higher pressures. The absorbance was recorded at the wavelength of maximum absorption for each tautomer at least three times to obtain an average value (standard error ± 2% at higher pressures; ± 5% at pressures below 730 psig). The pressure varied less than 1.5 psi within a single

spectral scan, and data were taken with increasing pressure to ensure that the solute concentration remained constant. Since single beam spectroscopy was used in this double beam apparatus, blank runs (no Schiff base) were made for each solvent system at every pressure point, and this subsequent spectrum was subtracted from the spectrum which contained the Schiff base.

The high-pressure cell was loaded with a solution of 20 μl of (0.0437 M) Schiff base in acetone using a syringe to obtain a probe concentration of 1.5×10^{-4} M, which is below the solubility limit at experimental conditions as determined spectroscopically. The cell was flushed with multiple volumes of low pressure ethane to evaporate the acetone and to displace air from the system. In the experiments without cosolvent, the cell was then pressurized with ethane to the desired initial pressure. In cases where cosolvent was added, the cell was charged with 100 psig of ethane after removing air from the system. Then, the cell was isolated from the rest of the system, and the lines leading to the cell were pressurized with 450 psig of ethane. The external sample loop was then rinsed and filled with the cosolvent, and the sampling valve and the valve leading to the cell were opened simultaneously to force the cosolvent into the cell using the pressure differential. The cell was further pressurized with ethane to the desired pressure set point, and after equilibration of temperature and pressure, absorbance spectra were measured as described above.

Calculation of K_C

The equilibrium constant (K_C) was calculated from the following equation:

$$K_c = \frac{c_{keto}}{c_{enol}} \qquad (1)$$

where c_{keto} is the concentration of the keto tautomer and c_{enol} is the concentration of the enol tautomer. Concentration is related to the measured absorbance through Beer's law, thus,

$$K_c = \left(\frac{\varepsilon_{enol}}{\varepsilon_{keto}}\right)\left(\frac{A_{\lambda \max.keto}}{A_{\lambda \max.enol}}\right) \qquad (2)$$

where A represents the absorbance at the maximum wavelength for each tautomer for a given solvent system. The ratio of extinction coefficients and absorbances were obtained as described previously. The wavelength of maximum absorption changes for the various cosolvent modified SCF solutions due to solvochromatic shifts.

Results and Discussion

The experimental equilibrium constant was found to be a function of cosolvent acidity, cosolvent concentration, and density. Polar cosolvents such as acetone, chloroform, and dimethylacetamide (DMA) did not affect the position of tautomeric equilibria. Only cosolvents capable of hydrogen bonding (EtOH, TFE, and HFIP) led to any significant amount of Schiff base tautomerization; the equilibrium constant shifted towards the keto tautomer in the presence of cosolvents which were capable of forming hydrogen bonds. The equilibrium constant also increased with increasing acidity of the cosolvent as can be seen in Figure 4.

The equilibrium constant was also found to shift substantially with varying amounts of cosolvents as can be seen in Figure 5 with the TFE modified SCF ethane solvent system.

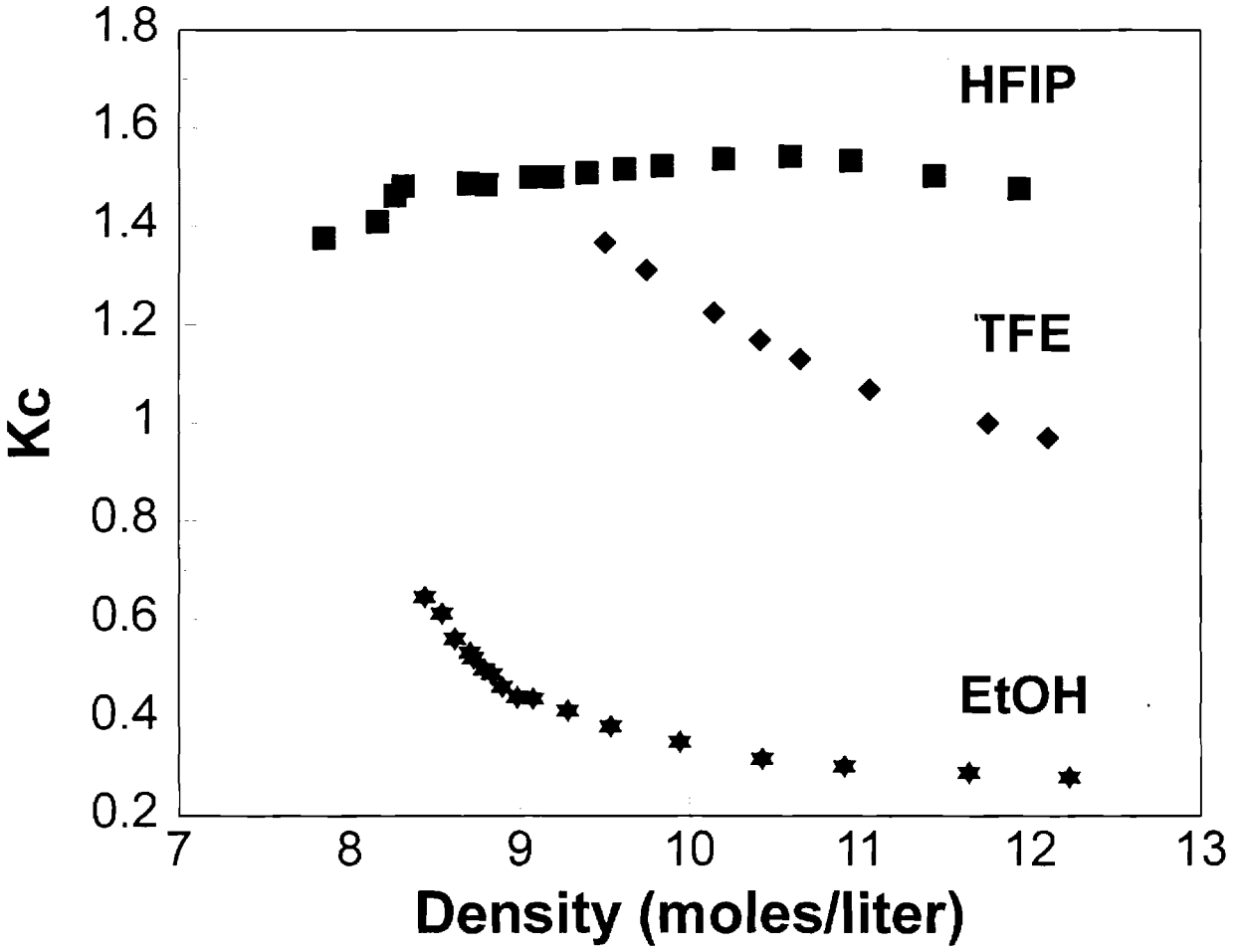


Figure 4. Equilibrium constant (K_c) as a function of density for approximately 0.1 M cosolvent (EtOH, TFE, HFIP) in SCF ethane. (Equilibrium constant (K_c) as a function of density for approximately 0.1 M cosolvent in SCF ethane.)

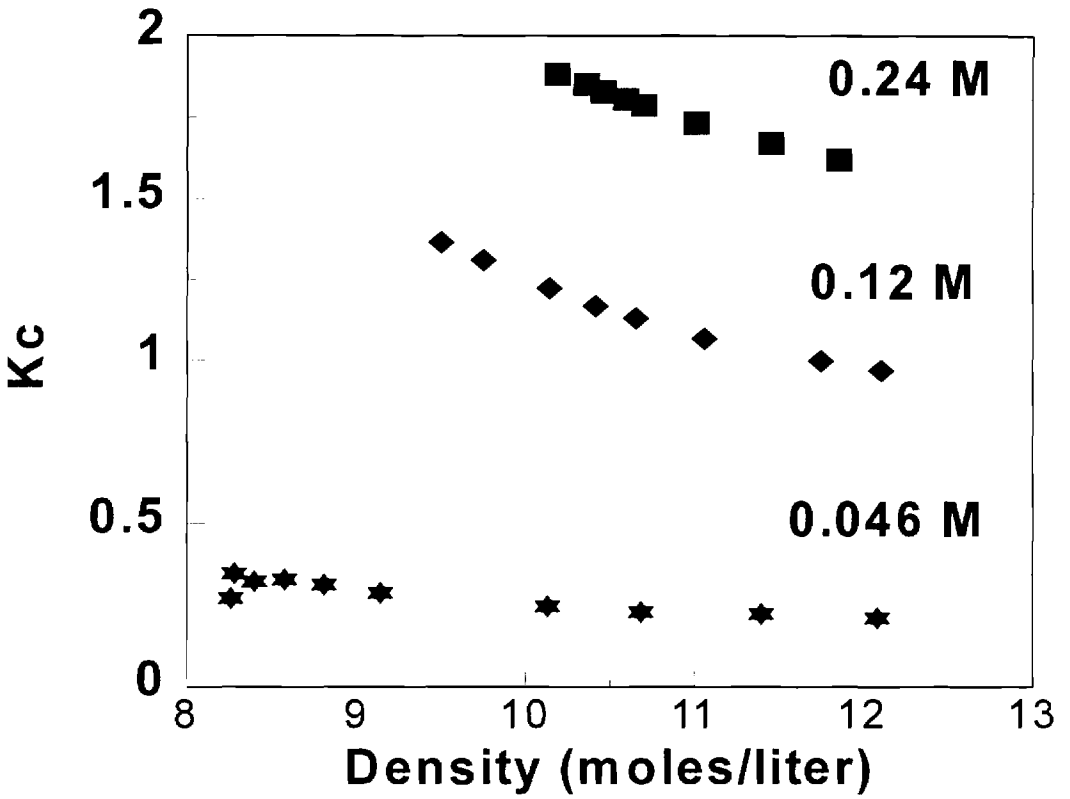


Figure 5. Equilibrium constant (K_c) as a function of density for 0.046 M, 0.12 M, and 0.24 M TFE in SCF ethane. (Equilibrium constant (K_c) as a function of density for Schiff base in TFE modified SCF ethane.)

It is important note that miscibility limits and critical mixture densities are different for each cosolvent system and for each cosolvent concentration; therefore, experimental data do not all begin at the same density. The same trend of shift in equilibrium constant was also found with ethanol and HFIP as cosolvents.

These results indicate large changes in tautomerization equilibrium may be obtained with small amounts of carefully selected cosolvents; however, the most interesting and informative result is the variation of the equilibrium constant with density. This effect can be seen in Figure 6 for ethanol and TFE modified SCF ethane solvent

systems. The ethanol cosolvent system exhibits the largest density dependence. In all cases, the lowest concentration of added cosolvent results in a larger density effect on the equilibrium constant than the corresponding higher cosolvent concentrations. At the lowest cosolvent concentrations, miscibility limits permit the experiment to extend into the near-critical region of pure SCF ethane where local composition enhancements due to solute-solvent or solute-solute clustering are significant. At the higher concentrations, the experiments are further removed from this near-critical, compressible region. In addition, the shift in equilibrium constant towards the keto tautomer in the lower density regions may be enhanced by the reduction in self-association of the alcohols which occurs in this same region. These free alcohols have a greater tendency to form intermolecular hydrogen bonds with the keto tautomer.

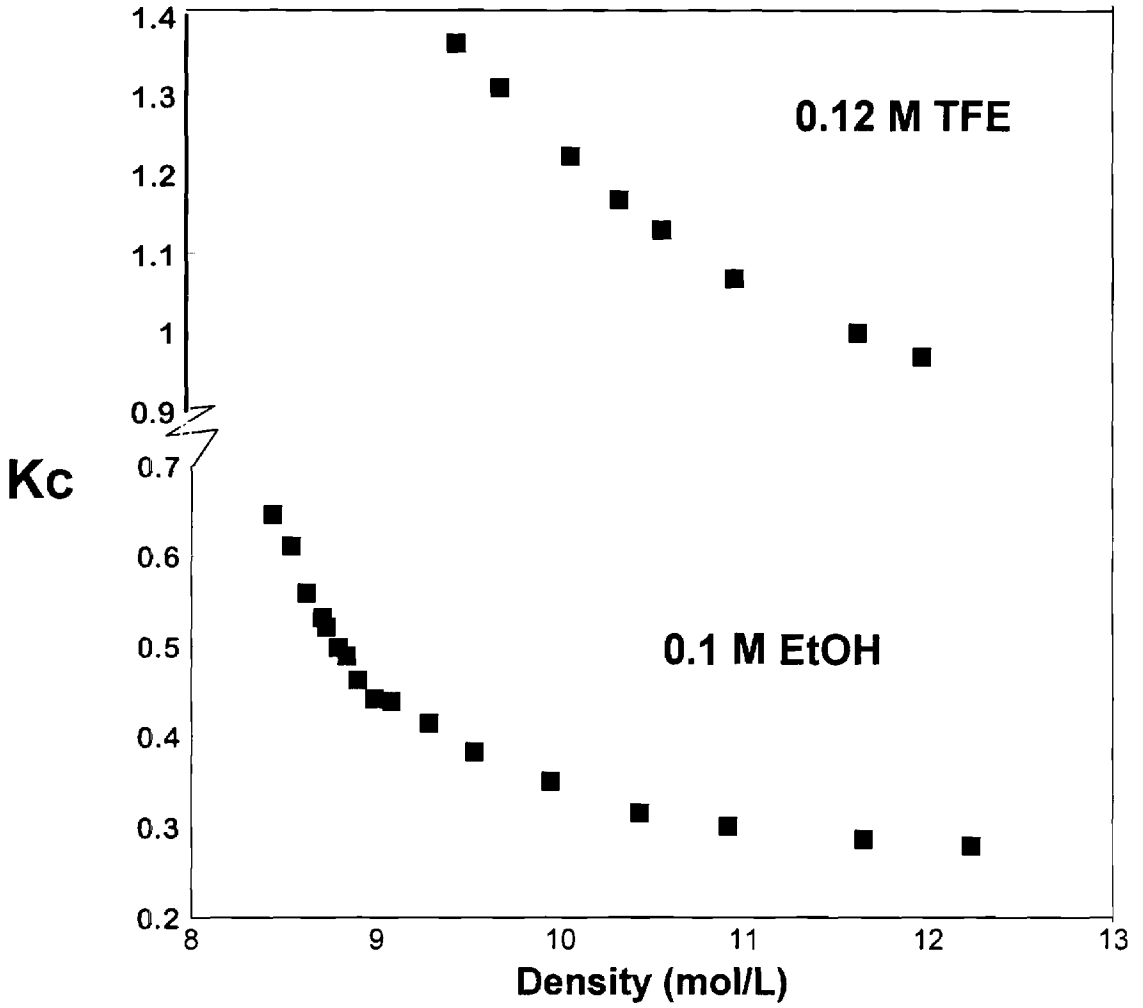


Figure 6. Equilibrium constant (K_c) as a function of density in cosolvent/SCF ethane in 0.1 M ethanol and 0.12M (Equilibrium constant (K_c) as a function of density in several cosolvent/SCF ethane systems.)

Therefore, the density effect observed can be attributed to a combination of factors. First, even in a compressed gas far from its critical point, density changes cause shifts in chemical equilibria due to changes in fugacity. However, in the near critical fluids we also have large effects due to local density and composition enhancements. Finally, hydrogen bonding of the keto tautomer to the cosolvent prevents tautomerization back to the enol form. As pressure is increased beyond the critical region, the

equilibrium constant of hydrogen bonding decreases (Gupta et al., 1993; Kazarian et al., 1993a; Kazarian et al., 1993b), which would reduce the concentration of the hydrogen bonded keto form and result in a decrease in the equilibrium constant.

Modeling Based on General Chemical Physical Analysis

A physical-chemical model has been developed to characterize the behavior of the equilibrium constant as a function of density. Possible equilibria describing this solute in a cosolvent modified solvent system are shown below. The equilibrium constant K_1 is the actual tautomerization between the keto and enol forms of the Schiff base. The equilibrium constants K_2 and K_3 indicate the equilibrium between the cosolvent, a hydrogen bond donor, and the Schiff base tautomers which are hydrogen bond acceptors, along with the hydrogen bonded complex of each form. Finally K_4 is the equilibrium constant for the dimerization of the alcohol cosolvents. Other equilibria such as the formation of the higher self-associates of the alcohol cosolvents are neglected. In addition, HFIP exists in an equilibrium between two rotamer forms which have slightly different acidities. This equilibrium is know to vary with density (Kazarian and Poliakoff, 1995), however, should have negligible effects on the Schiff tautomerization and will be ignored.

$$\begin{aligned} K &\overset{K_1}{\leftrightarrow} E \\ K + H &\overset{K_2}{\leftrightarrow} KH \\ E + H &\overset{K_3}{\leftrightarrow} EH \\ H + H &\overset{K_4}{\leftrightarrow} HH \end{aligned} \tag{3}$$

Where K , E, and H designate the keto tautomer, enol tautomer, and cosolvent, respectively.

For simplification, only cosolvent systems with minimal self-association were modeled. The self association of fluorinated alcohols such as TFE is minimal, and with HFIP, there is essentially no dimerization at the concentrations used (Schrems et al., 1992; Kazarian et al., 1993b; Marco et al., 1994). Additionally, it was found from gas phase hydrogen bonding data between the fluoro-alcohols and various ketonic and enolic (phenolic, in particular, such as the enol form of the Schiff base used in this investigation) compounds that the third equilibrium (K_3) may be ignored (Abraham, 1993; Marco et al., 1994) because the equilibrium constant for hydrogen bonds between fluoro-alcohols and ketones is so much greater in comparison to that between the fluoro-alcohols and the phenolic compounds. This results in a model based on only two equilibrium constants:

$$K_1 = \frac{z_K \phi_K}{z_E \phi_E} \tag{4}$$

$$K_2 = \frac{z_{KH} \phi_{KH}}{z_K \phi_K z_H \phi_H} \tag{5}$$

where z_K, z_E, and z_{KH} are the true concentrations of the keto and enol tautomers of the Schiff base, respectively, and the keto hydrogen bonded complex; and the ϕ_K, ϕ_E, and ϕ_{KH} are the fugacity coefficients for these species.

In order to compare the model directly to the experimental results, an expression in terms of the experimental equilibrium constant was derived. For this derivation, it was

assumed that the fugacity coefficients for each of the free Schiff tautomers (ϕ_K and ϕ_E) were equal and the free cosolvent concentration was constant, because in all cases the added cosolvent was in great excess of the Schiff base concentration. Then, the experimental equilibrium constant is given by,

$$K_{C,\exp} = \frac{\left[c_K + c_{KH}\right]}{\left[c_E\right]} \tag{6}$$

where the concentration of the keto tautomer is now a combination of the free and hydrogen bonded form of the tautomer. Then, the equilibrium constant calculated from a physical-chemical analysis becomes,

$$K_{C,calc} = K_1(1 + K_2 C_{cos}\phi^*) \tag{7}$$

where

$$\phi^* = \frac{\phi_K \phi_H}{\phi_{KH}}, \tag{8}$$

K_1, K_2 are defined previously in equations 4 and 5, and C_{cos} is the bulk cosolvent concentration.

The fugacity coefficients were calculated from the Peng-Robinson equation of state (Reid et al., 1987). The binary interaction parameters (k_{12}) for the cosolvent/ethane systems were regressed from measured mixture densities and are given in Table 2. The binary interaction parameters for the cosolvent/Schiff complex in SCF ethane (k_{14}) arbitrarily were set equal to those for the cosolvent The binary interaction coefficient for the Schiff base/ SCF ethane (k_{13}) were set equal to 0.1 and all other interaction parameters were set equal to zero. The critical properties of ethane, ethanol (Reid et al., 1987), and TFE (Suresh et al., 1994) were obtained from the literature. The critical temperatures of

HFIP, Schiff base, and Schiff base/cosolvent hydrogen bonded complex were estimated from Fedor's method; the critical pressure and volume for the same compounds were estimated using the Joback method; and the acentric factor was estimated from the critical volume (Reid et al., 1987).

Table 2. Binary interaction parameters for SCF ethane/cosolvent systems regressed from experimental data using the Peng-Robinson equation of state.

Cosolvent in SCF Ethane	**Cosolvent Composition (mol%)**	k_{ij}
TFE	0.98	0.055
TFE	1.98	0.194
HFIP	0.68	-0.053
HFIP	1.36	0.033
EtOH	1.7	0.061

The equilibrium constant for the Schiff base keto tautomer/cosolvent hydrogen bonded complex (K_2) was assumed to be equal to the gas phase equilibrium constant for the same hydrogen bond donors with similar ketone compounds . These were obtained from the literature (Marco et al., 1994) and are given in Table 3. The gas phase data were given for 25 °C and were corrected to experimental conditions of 35 °C using gas phase enthalpy of formation literature data for the appropriate cosolvent/ ketone complex (Kivinen and Murto, 1969; Tucker and Christian, 1976). The equilibrium constant of tautomerization for the free Schiff base in the keto and enol forms was fit to the

experimental data at the highest pressure data to avoid the effect of the anomalous behavior associated with the SCF critical region is absent.

Table 3. Equilibrium constants (K_2) for keto Schiff base/cosolvent hydrogen bonded complex at 25°C and corrected to 35°C.

Schiff Base/Cosolvent Hydrogen Bonded Complex	K_2 (L/mol) 22°C	K_2 (L/mol) 35°C
TFE	53	37
HFIP	250	154

The results of the model for the highest and lowest cosolvent concentration of TFE and HFIP are shown in Figures 7 and 8. With both cosolvent systems, the model agrees with the experimental data much better at the highest cosolvent concentration. In all cases, however, the model diverges from the experimental data in the area closest to the critical region. The model takes into account the changes in the K_C which result from changes in solution fugacity. Therefore, it is likely that the differences between the theory and the experimental data are a result of solute-cosolvent clustering resulting from local composition enhancements and increases in hydrogen bonding approaching the critical region.

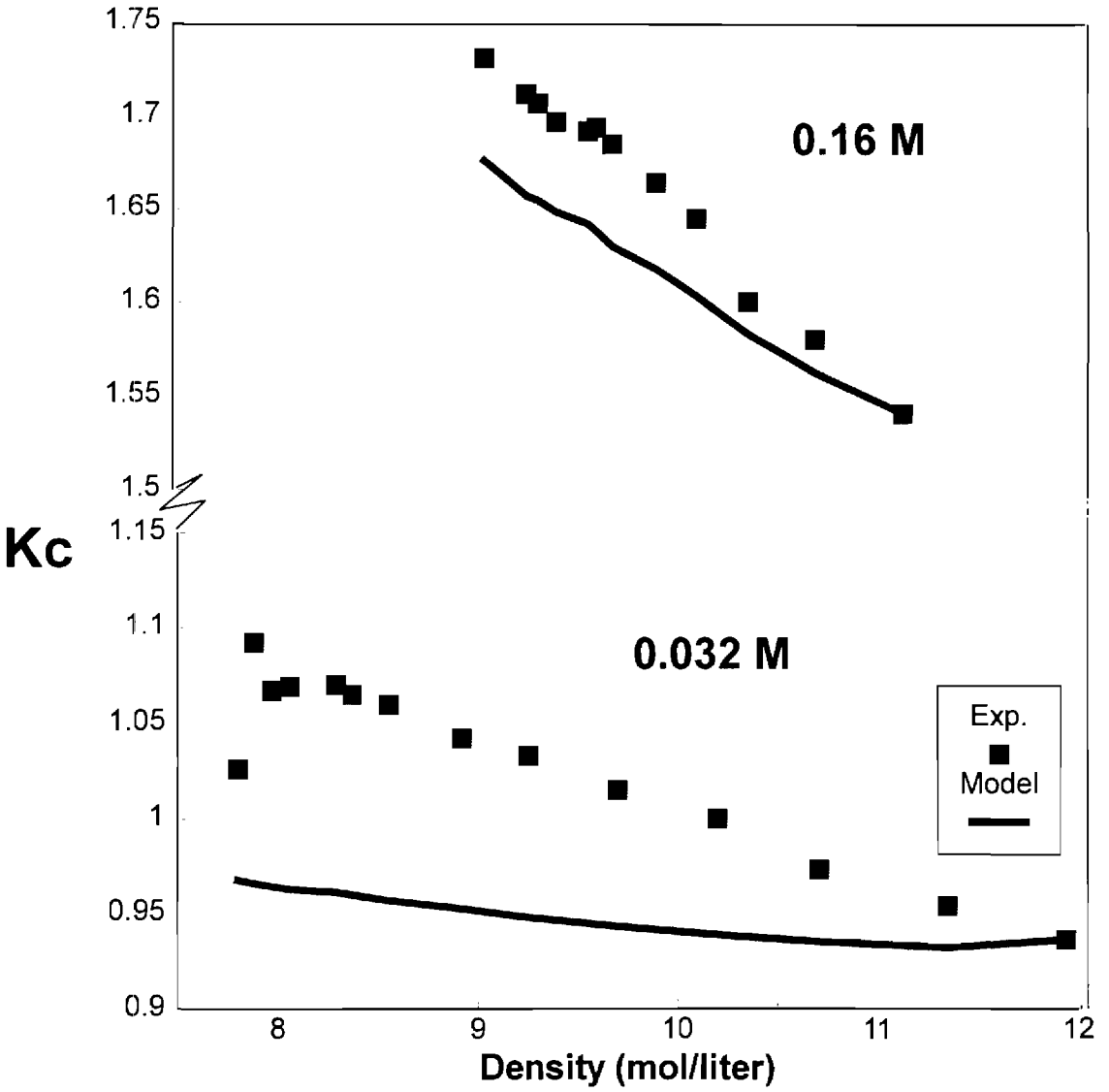


Figure 7. Results of equilibrium model:) 0.046 M and 0.24 M TFE/SCF ethane at 35°C. (Results of equilibrium model for Schiff base in TFE/SCF ethane solvent system.)

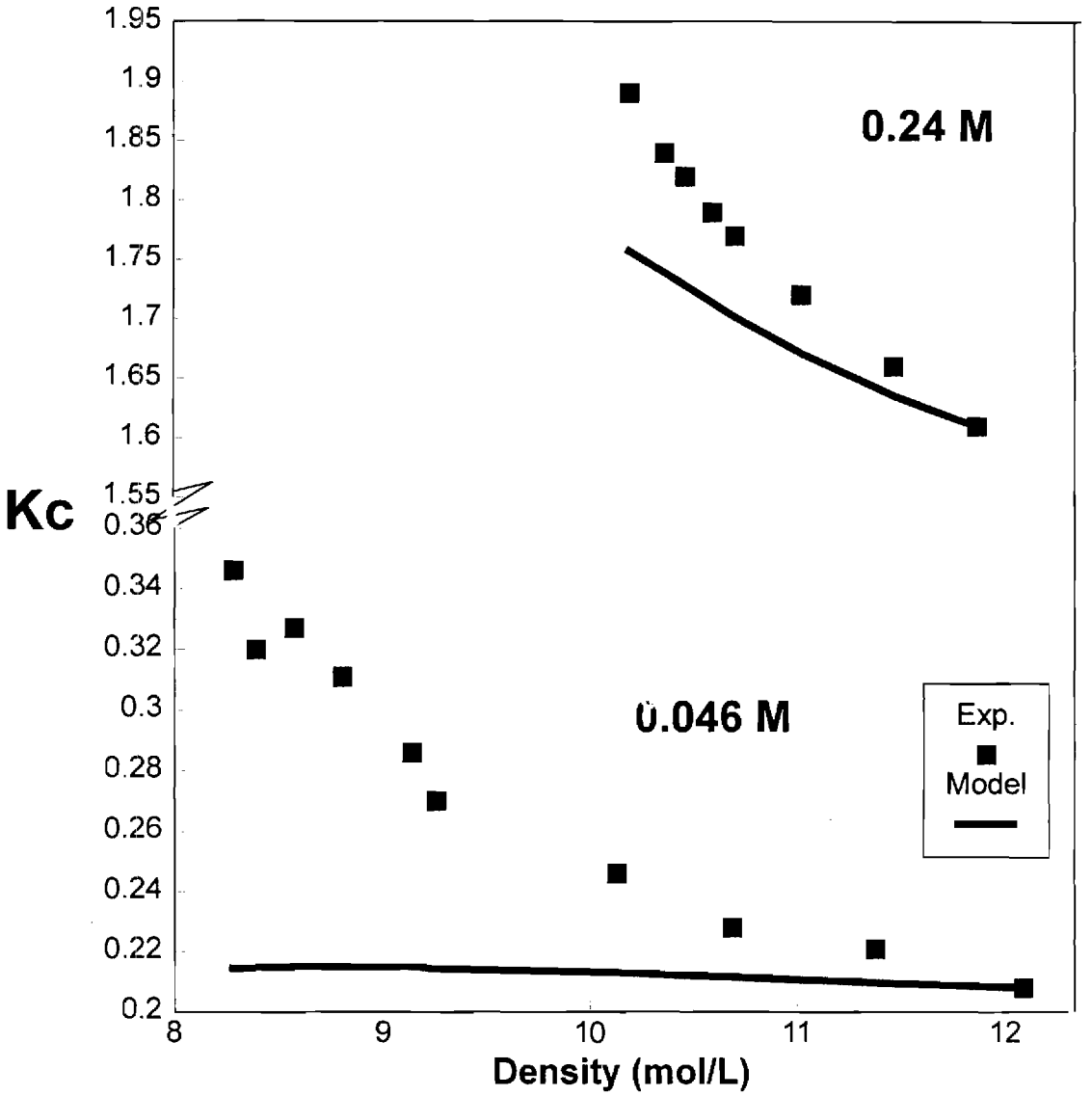


Figure 8. Results of equilibrium model: 0.032 M and 0.16 M HFIP/SCF ethane at 35°C. (Results of equilibrium model for Schiff base in HFIP/SCF ethane solvent system.)

A sensitivity analysis of the variables associated with the prediction of the equilibrium constant was performed to ensure that the differences between predicted and experimentally measured data were not due to inaccuracies in estimated values and literature constants. From the perturbation of estimated and literature values, it was found that the only variable in the model which could account for the magnitude of the

discrepancy between the model and experiment was the cosolvent concentration. The local concentration of cosolvent needed for the model and experimental data to agree at the lowest density point for each data set is given in Table 4. The local composition enhancement needed for this local concentration is also given in this table. For both cosolvent/SCF systems modeled, the local concentration of cosolvent around the Schiff base is equal (within experimental error) for the highest and lowest bulk cosolvent concentrations. This is consistent with the possibility of saturation of the local cosolvent concentration about the Schiff solute.

Table 4. Local composition enhancement and local concentration of cosolvent about the Schiff base from modeled results using chemical-physical theory.

Cosolvent	Bulk Concentration (M)	Mole Fraction Ratio x_{local}/x_{bulk}	Local Concentration (M)
TFE	0.046	9.2	0.423
TFE	0.24	1.7	0.401
HFIP	0.032	6.5	0.208
HFIP	0.164	1.3	0.213

There are several possible explanations for the observations above. At the highest cosolvent concentrations, miscibility limits dictate that the experiments are carried out beginning at densities which are well removed from the near critical region of the solvent system. In the cases of the lowest cosolvent concentrations, it was possible to extend the spectroscopic measurements into the critical region of the solvent system without phase splitting, where local composition enhancements are known to occur. In addition, with

nearly 2 mol% of added cosolvent, the fluid is much less compressible in general than at lower cosolvent concentrations. It is also known that the equation of state fugacity coefficient calculations are more accurate at pressures well removed from the critical region.

II) DIELS-ALDER REACTION OF ANTHRACENE AND PTAD

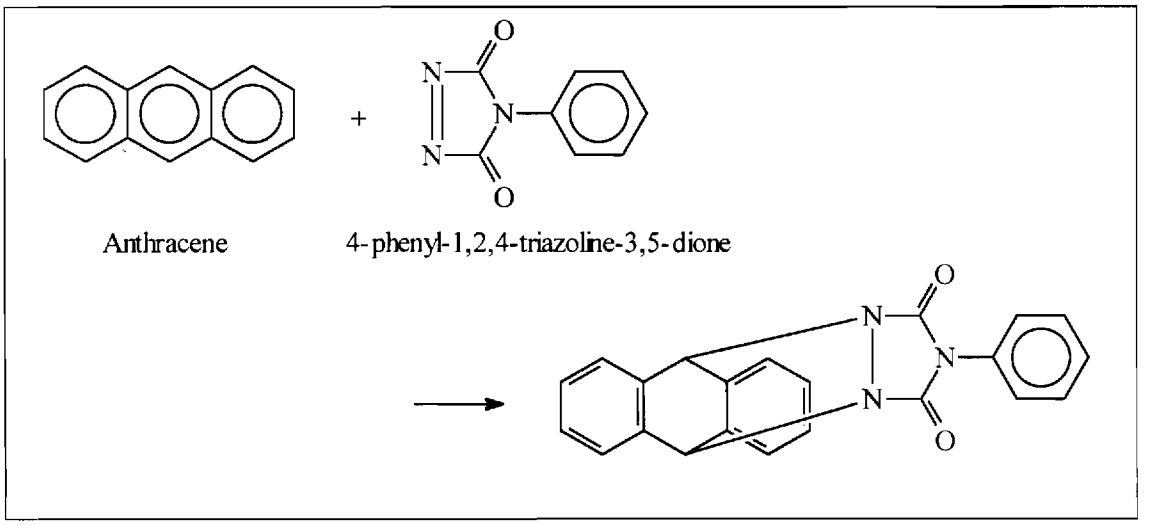
Over the last two decades, supercritical fluids have received an increasing amount of attention as a medium for carrying out chemical reactions (Savage, et al., 1995). The interest stems from unique advantages that supercritical fluids provide in the area of reaction rate control. A supercritical fluid, defined as a material at conditions above its critical temperature and pressure, is highly compressible at conditions near its critical point. The compressibility of the solvent can lead to large changes in reaction rate over small changes in pressure, and since pressure can be manipulated easily and precisely, pressure tuning represents a convenient route to rate control. Additional control of reaction rate can often be achieved through modification of the supercritical solvent with small amounts of a second solvent, designated as a cosolvent.

Among supercritical solvents, CO_2 has received special attention due to the fact that, in addition to a density which can easily be tuned over an order of magnitude, it also provides a compelling combination of low cost, an easily accessible, thermally mild critical point, and low toxicity. This combination of attributes is especially attractive to the food and pharmaceutical industries.

The reactants used to produce the rate data in this work follow a Diels-Alder reaction pathway, but the dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), is atypical. The reactive part of PTAD's structure is identical to maleimide, but has a pair of nitrogens at the bonding site instead of carbons. The reaction is illustrated in Figure 9.

The nitrogen substitution results in reaction rates an order of magnitude higher than maleimide (Konovalov, et al., 1979), and has allowed the data presented in this work to be collected relatively swiftly. PTAD possesses another attractive aspect in addition to its high reactivity, and that is the fact that, as a member of the Diels-Alder class of reactions, it is an elementary, bimolecular reaction with a well established mechanism (Sauer, 1967). This allows the rate constant to be measured using simple pseudo first order data reduction techniques.

Figure 9. The Diels-Alder reaction of anthracene (diene) with 4-phenyl-1,2,4-triazoline-3,5-dione (dienophile.)



PROCEDURE

Reaction kinetics were followed spectroscopically by fluorescence. The equipment used to make these measurements was configured in the manner illustrated in

Figure 10. Light from a Spectral Energy SX1000-2 Xenon UV lamp was passed through a Kratos Analytical Model GM252 monochromator, producing an excitation light beam

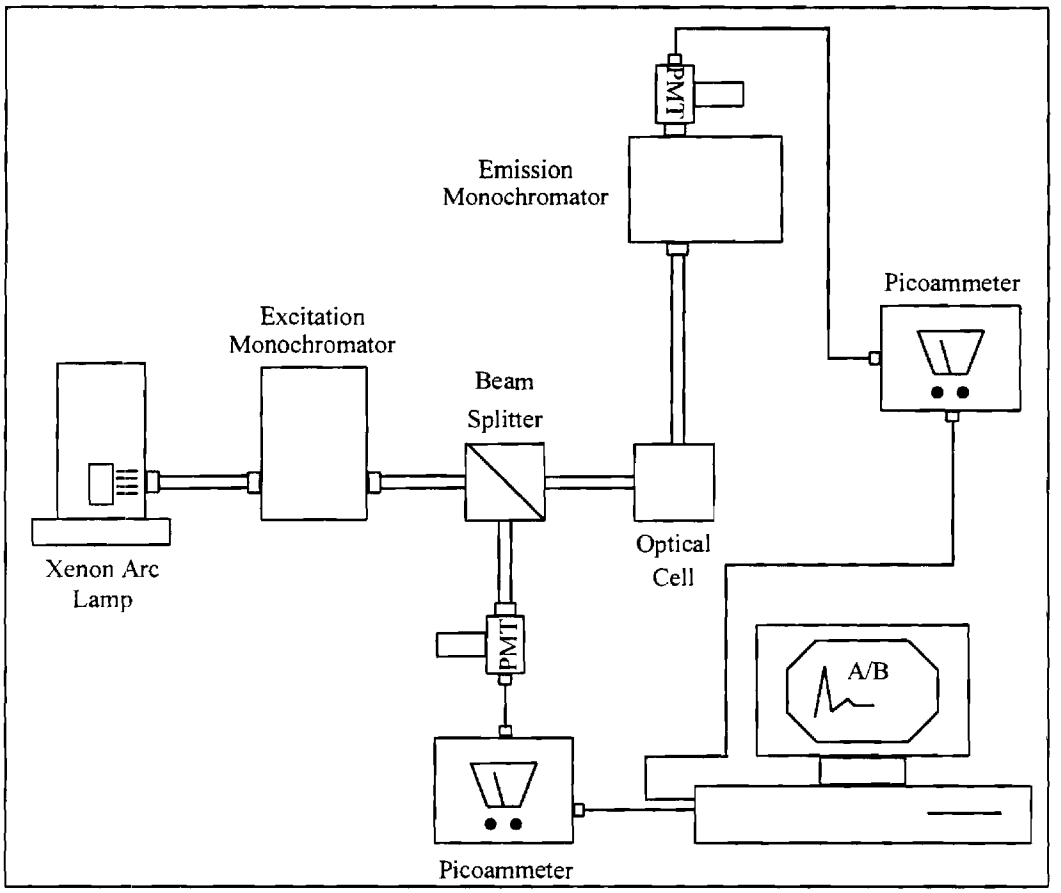


Figure 10. An overview of the high pressure fluorescence apparatus used for kinetic measurements.

at a single wavelength. The excitation beam was split into two beams using a half-silvered mirror, producing an excitation beam and a reference beam.

The reference beam was directed into a Kratos D 500 Side-On Photomultiplier Tube (PMT), which produced an amperage output measured using a Keithley Instruments 414A Picoammeter. The excitation beam was directed into the optical cell containing the experimental sample of anthracene. The fluorescence of anthracene produced an

emission beam of light, which was directed into a second GM252 monochromator where it was filtered to a single wavelength of light. The filtered emission wavelength was directed into a second D 500 PMT, which produced an amperage output that was measured using a Keithley 485 Autoranging Picoammeter.

Each picoammeter produced an analog output voltage in proportion to beam intensity, designated as Signal A for the emission beam intensity and as Signal B for the reference beam intensity. The ratio of these two signals - A/B - varied with changes in fluorescent emission intensity, but it did not vary with fluctuations in lamp intensity. The emission intensity of the sample was recorded as the numerical value of the ratio A/B.

The optical cell was constructed from 316 stainless steel and was configured for solvent introduction and removal as in Figure 11. The windows were made from quartz, and were positioned at right angles to one another so that as little of the excitation light as possible would exit the cell with the emission light. The seals for cell windows were o-rings made of Teflon. All tubing and fittings were stainless steel and were manufactured by Swagelok or HiP. CO_2 was delivered to the cell using an ISCO Model 260D syringe pump, which fed through a Valco 6-port sample injection valve. A Teflon coated stirbar was used to provide agitation of the cell contents.

Pressure was measured using a Druck PDCR 911 transducer attached to a Druck DPI 60 digital readout. The pressure transducer and readout were calibrated using a Ruska dead weight calibration apparatus, and were found to be accurate to +/- 1 psi.

Internal temperatures were measured using a 1/16" grounded Omega Type K thermocouple in an inconel sheath. It was mounted with its tip in direct contact with the reactant solution. The thermocouple was attached to a readout with resolution to 0.1°C.

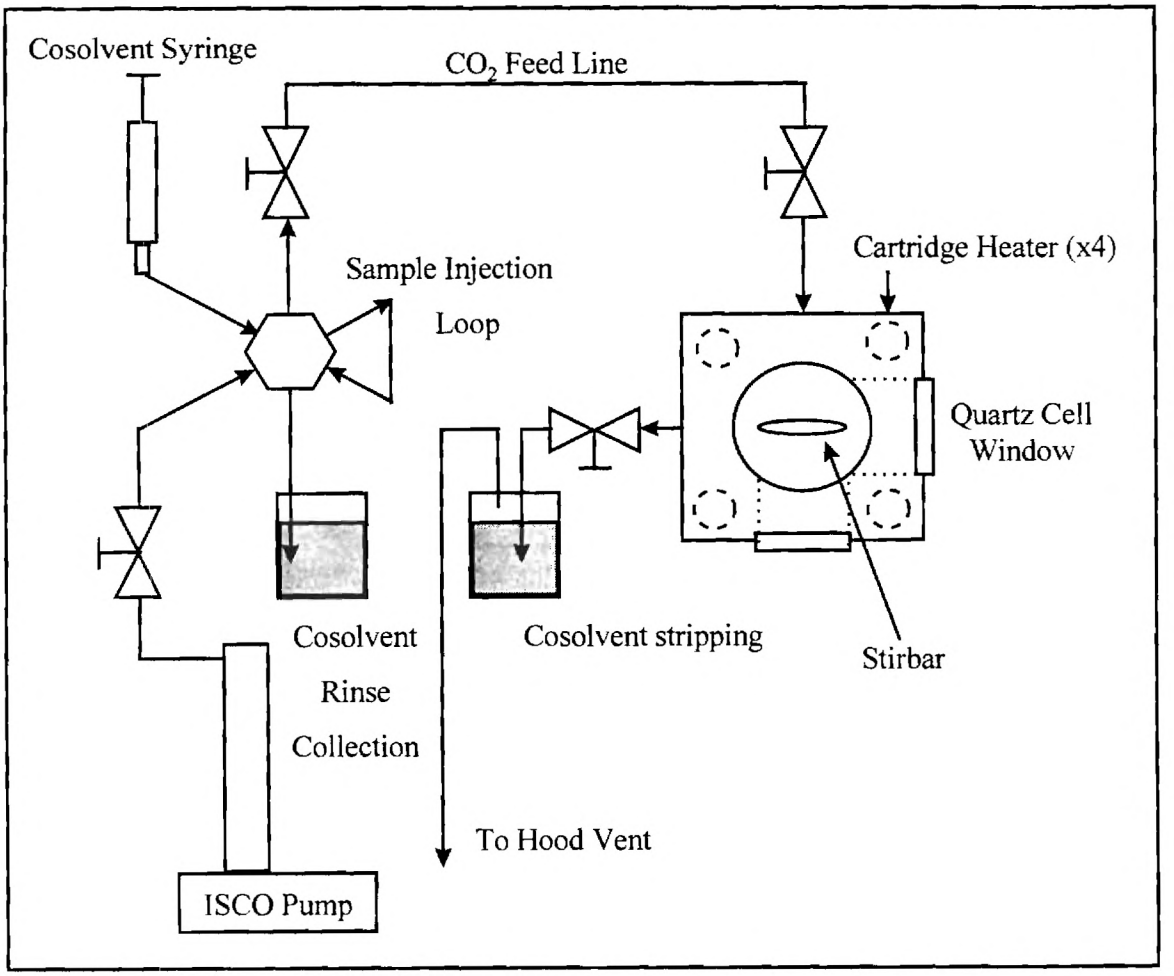


Figure 11. An overview of the optical cell and the apparatus used for the injection of cosolvents.

The thermocouple was calibrated against a platinum resistance thermometer, and was found to be accurate to +/- 0.1°C.

Internal temperature was controlled using a second 1/8" Type K thermocouple mounted with its tip in the steel of the cellblock. The thermocouple was attached to an

Omega CN9000A controller which used four cartridge heaters mounted in the steel of the cell block to maintain cell temperature. Temperature control of cell contents was within +/- 0.2°C.

Kinetic Analysis

The reaction of PTAD with anthracene is an elementary bimolecular reaction, so, if one reactant is present in excess, pseudo first order kinetics can be used to extract rate constants from concentration versus time data. UV spectroscopy was used for the analysis of the reaction rate of PTAD and anthracene in liquid solvents (Konovalov, Breus et al. 1979) by following the decay of PTAD over time. In order to apply pseudo first order kinetics, anthracene needs to be present in excess. Though an excess of anthracene is possible in liquids, PTAD solubility in supercritical CO_2 is on the order of 10^{-3} mol/L, and anthracene solubility is on the order of only 10^{-5} mol/L. The dilemma was solved by using fluorescence spectroscopy instead of UV. Fluorescence spectroscopy can detect concentrations of anthracene as low as 10^{-7} mol/L, making it possible to have PTAD present at an initial excess of 100:1 and still follow a change in anthracene concentration over two orders of magnitude.

In order to calculate the rate constant of the reaction conveniently from fluorescence emission data, it was possible to use Beer's law to relate pseudo first order rate constants directly to changes in emission signal. Solution of the differential equation (9) relating concentration changes of one reactant to the concentration of both reactants leads to (10) when PTAD is assumed to be in great excess and therefore constant throughout the reaction.

$$\frac{dc_{AN}}{dt} = k_c c_{PTAD} c_{AN} \qquad (9)$$

$$\ln\left(\frac{c_{AN}}{c_{ANo}}\right) = -\left(k_c c_{PTADo}\right)t \qquad (10)$$

Simple experiments involving incremental additions of anthracene to a liquid solvent indicated that the fluorescence of anthracene follows Beer's Law (11) as long as the anthracene is dilute (i.e. less than 10^{-5} mol/l), and the emission wavelength monitored is well removed from wavelengths at which self-absorption may occur. The path length "l" in Beer's Law does not change during a run, so (11) may be written once for initial conditions and again for an arbitrary time t. The ratio of these equations may be substituted into (10), leading to (12). Equation (12) allows the pseudo first order rate constant to be derived directly from emission data without knowing the exact concentration of anthracene in the cell.

$$e = \varepsilon l c_{AN} \tag{11}$$

$$\ln\left(\frac{e_{AN}}{e_{ANo}}\right) = -k_c c_{PTADo} t \tag{12}$$

Kinetic Measurements in Pure Supercritical CO_2

Stock solutions of PTAD and anthracene were prepared in acetone. A fresh PTAD stock solution was prepared each day. A known quantity of each stock solution was placed into the optical cell using a Gilman Pipet, with PTAD in excess by a factor of 40. The cell was dried under vacuum for 5 minutes. Care was taken to insure that the two stock solutions did not contact one another during drying. Dryness of the cell was determined by visual inspection.

Data acquisition software was started, and the cell was pressurized with pure CO_2 from the ISCO syringe pump. The time and pressure at which the cell reached the desired temperature was recorded, and the reaction was observed for about twenty minutes. Kinetic analysis was performed only on data collected while the cell was at within +/- 0.2°C of the desired temperature. The cell was cleaned thoroughly with acetone between each experiment.

Modeling of Kinetic Data in Pure Supercritical CO_2

Rate constants were previously obtained for the reaction in pure CO_2 at 40°C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 216 bar. Rate constant

values are plotted in Figures 12 and 13. Two views are provided for the purpose of making the cluster of points at 95 bar more readable. Near the critical temperature, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are as much as 26 times greater than those above 110 bar. The average estimated error in rate constant values was 20% at higher pressures, increasing to as much as 70% near the critical pressure.

The drop in rate constant with increasing pressure is similar to the result obtained for the esterification of phthalic anhydride with methanol in supercritical CO_2 [Brennecke, et al, 1994]. The bimolecular rate constant for the phthalic anhydride reaction also decreased at pressures above the critical pressure and produced rate constant enhancements near the critical pressure similar in magnitude to those observed for the PTAD reaction. Brennecke estimated the local concentration of methanol around a phthalic anhydride molecule using an analogy with solvatochromic work using phenol-blue [Johnston, 1987 #58]. She determined that, in the region near the critical pressure, local concentration was higher than bulk concentrations by a factor of 5. When this increase in local concentration was accounted for, and rate constants were calculated using local concentration values, the reaction showed only a slight sensitivity to pressure in the region near the critical pressure.

Figure 12. Rate constants for the reaction of PTAD with anthracene in pure CO_2 at 40°C.

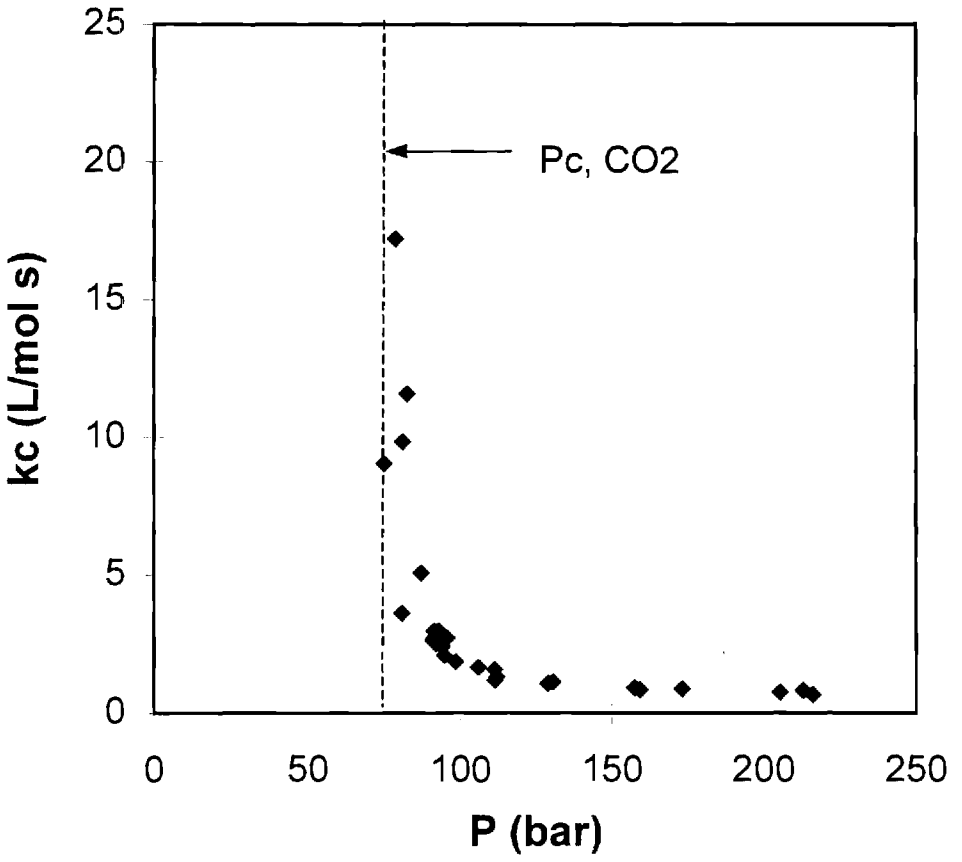
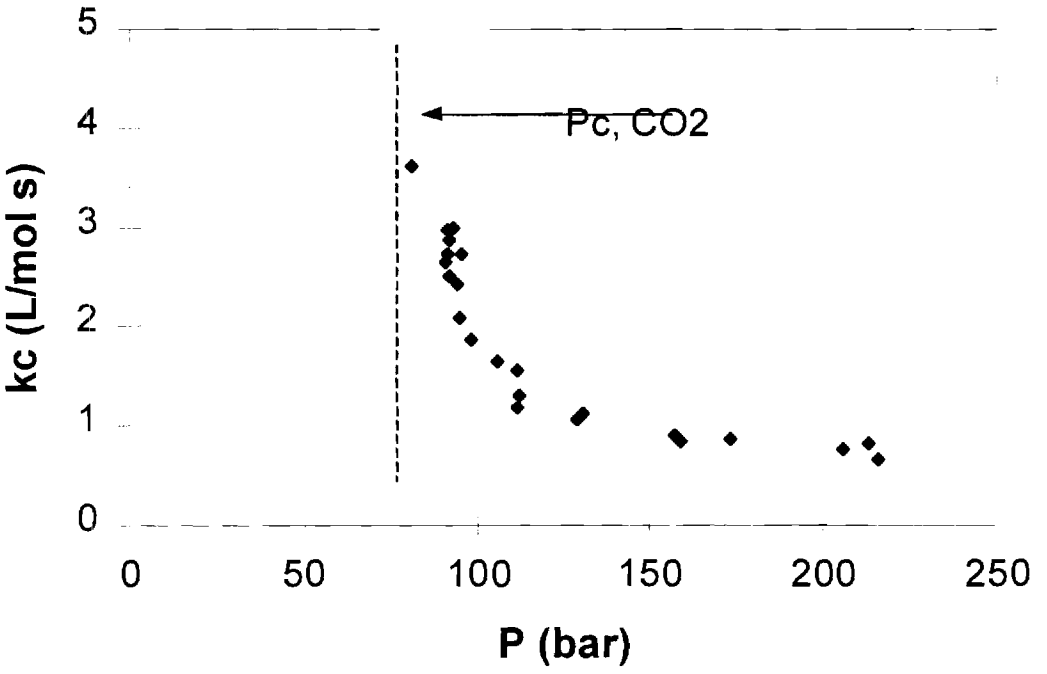


Figure 13. Rate constants having values less than 5 l/mol s for the reaction of PTAD with anthracene in pure CO_2 at 40°C.



In order for a local concentration increase to occur in the reaction of PTAD with anthracene, it is necessary for solute-solute clustering to be present along with solute-solvent clustering. Evidence for solute-solute clustering in dilute solutions is found in work by Kurnik [Kurnik, 1982 #98], so clustering effects on local concentrations are one possible explanation of the rate constant trends found in this work.

The construction of mathematical models capable of predicting these kinetic changes is now underway. The simplest promising avenue of investigation involves the assumption that the clustering effects are minimal, and that the kinetics may be successfully modeled as a function of changes in bulk fluid properties. The supercritical CO_2 can then be treated as a dense gas, which allows the following kinetic model based on high reference pressure fugacity coefficients to be derived (Eckert, 1974).

$$\frac{k}{k_o} = \frac{\phi_A \phi_B z}{\phi_M} \qquad (13)$$

Here. $\phi's$ are fugacity coefficients, and z is the usual compressibility factor of the gaseous mixture. Currently, a computer program for evaluating these fugacity coefficients at arbitrary pressures is being written. Evaluation of the fugacity coefficient model against experimental data using this program will continue into the next quarter.

Kinetic Data in Pure Supercritical CO_2 at 50°C

Rate constants were obtained for the reaction of PTAD with anthracene in pure CO_2 at 50°C and at pressures ranging from the critical pressure of CO_2 (73.8 bar) to 195

bar. Rate constant values at both 40°C and 50°C are plotted in Figure 14. At 40°C, the reaction shows great sensitivity to pressure in the region between the critical pressure and about 110 bar. Rate constants at the critical pressure are 25 times greater than those above 110 bar. At 50°C, the reaction rate constant shows only a slight change with pressure around the critical pressure. This slight increase in rate as pressure decreases is predicted by transition state theory (Evans and Polanyi, 1935; Brennecke, et al, 1994). The modest rate constants near the critical pressure indicate that molecular clustering is minimal at this temperature.

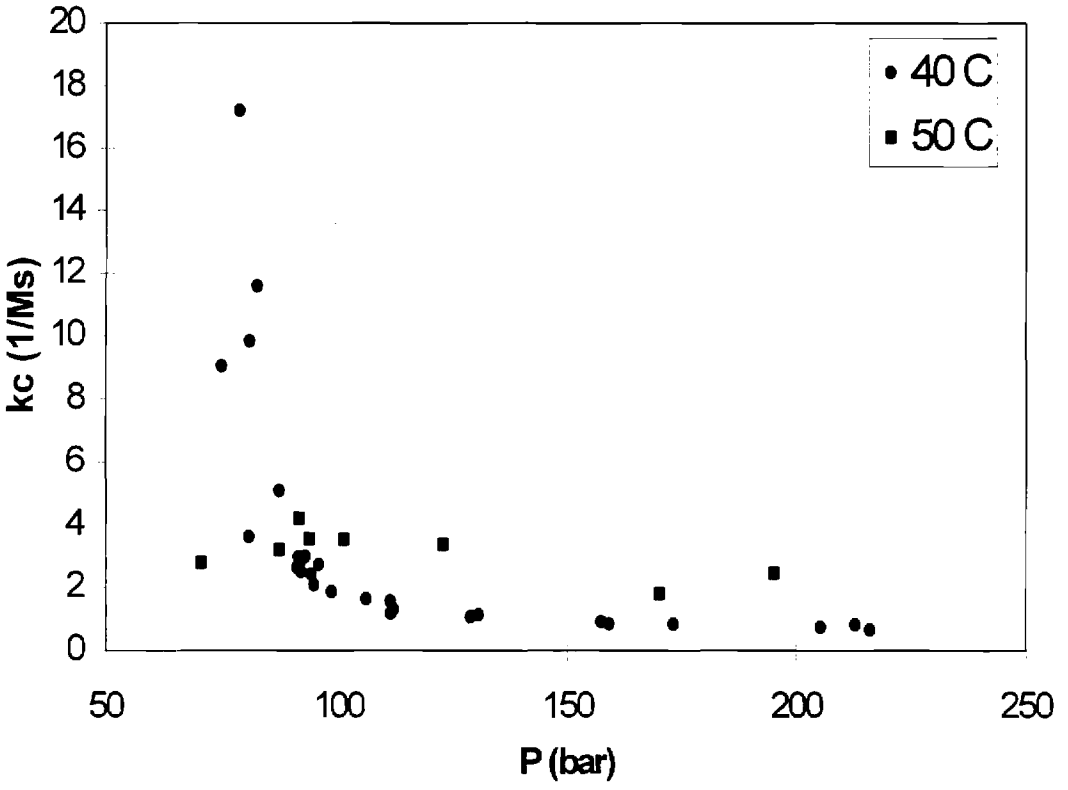


Figure 14. Rate constants for the reaction of PTAD with anthracene in pure CO_2 at 50°C.

CONCLUSION

Densities of binary supercritical mixtures of ethane with cosolvents, ethanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, have been measured by a constant volume apparatus. Measurements were made in the range 0.7 to 2.0 mol % cosolvent and pressure from 49.8 to 105.7 bar at 308.2 K. The tautomeric equilibrium constant was measured as a function of density in supercritical ethane modified with three different concentrations of hexafluoroisopropanol (HFIP). The measured equilibrium constant was found to be a function of fluid density and cosolvent concentration.

The position of Schiff base tautomeric equilibria was tuned from essentially one tautomer to another by modifying the solvent of pure SCF ethane with less than 2 mol% of cosolvents capable of hydrogen bonding interactions. For the cosolvents of EtOH, TFE, and HFIP, it was found that the equilibrium constant was a function of cosolvent concentration and mixture density. Modeling the equilibrium constants using general chemical-physical analysis results in differences in predicted and experimentally calculated equilibrium constants which are greater than accountable by theory alone. This evidence of solute-cosolvent clustering is consistent with the effects of density on hydrogen bonding (Kazarian et al., 1993). Hydrogen bonding has been shown to decrease with increasing density. A local composition enhancement of cosolvent about the Schiff base in the low density, near-critical region would result in an increased amount of hydrogen bonding which in turn shifts the equilibria to the keto tautomer. As the density of the solution is increased, the solute-cosolvent clustering decreases as the fluid becomes less compressible which also reduces the degree of hydrogen bonding.

This decrease in hydrogen bonding in turn affects the keto-enol equilibria by decreasing the amount of the keto formation. Thus, it is possible to utilize density dependence of hydrogen bonding in SCF solutions to "tune" tautomeric equilibrium between the keto-enol forms of the Schiff base.

Kinetic Diels-Alder data have been collected for pure CO_2 at 40°C and pressures between the critical pressure of CO_2 (73.8 bar) and 216 bar. These data support the theory of local density enhancements suggested in the literature. Data taken at 50°C and pressures ranging from 70 bar to 195 bar are also reported; they do not exhibit the molecular clustering evident closer to the critical temperature.

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